Partitioning Biological and Anthropogenic Methane Sources

by

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University Program in Ecology
Duke University

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Dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in the University Program in Ecology
in the Graduate School of Duke University
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Abstract

Methane (CH_4) is an important greenhouse gas, and an ideal target for greenhouse gas emissions reductions. Unlike carbon dioxide, CH_4 has a relatively short atmospheric lifetime, so reductions in CH_4 emissions could have large and immediate impacts on anthropogenic radiative forcing. A more detailed understanding of the global CH_4 budget could help guide effective emissions reductions efforts.

Humans have greatly altered the CH_4 budget. Anthropogenic CH_4 sources are approximately equal in flux to natural sources, and the current atmospheric CH_4 concentration is $\sim$2.5 times pre-industrial levels. The advent of hydraulic fracturing and resulting increase in unconventional natural gas extraction have introduced new uncertainties in the CH_4 budget. At the same time, the next few decades could be a crucial period for controlling greenhouse gas emissions to avoid irreversible and catastrophic changes in global climate. Natural gas could provide lower-carbon fossil energy, but the climate benefits of this fuel source are highly dependent on the associated CH_4 emissions. In this context of increasing uncertainty and growing necessity, quantifying the impact of natural gas extraction and use on the CH_4 budget is an essential step in making informed decisions about energy.

In the work presented here, I track CH_4 in the environment to address several areas of uncertainty in our present understanding of the CH_4 budget. I apply the tools of CH_4 analysis in a variety of environments, from rural groundwater supplies to an urban atmosphere, and at a range of scales, from individual point sources to

regional flux. I first show that carbon isotopes of CH_4 (δ^{13}C-CH_4) and co-occurrence of ethane (C_2H_6) are useful techniques for differentiating a range of CH_4 sources. In so doing, I also show that leaks from natural gas infrastructure are a major source of CH_4 in my study area, Boston, MA. I then build on this work by applying the same δ^{13}C-CH_4 and C_2H_6 signatures to partition CH_4 flux for the Boston metro region. I find that 88% of the CH_4 enhancement in the atmosphere above Boston is due to pipeline natural gas.

In the final portion of this thesis and the two appendices, I move from the distribution side of the natural gas production chain to extraction, specifically addressing the potential impacts from hydraulic fracturing in my home state of North Carolina. I combine the CH_4 source identification techniques of the previous sections with additional geochemical analyses to document the pre-drilling water quality in the Deep River Triassic Basin, an area which could be drilled for natural gas in the future. This data set is unique in that North Carolina has no pre-existing commercial oil and gas extraction, unlike other states where unconventional gas extraction is currently taking place. This research is, to my knowledge, the first to examine the hydrogeology of the Deep River Basin, in addition to providing an important background data set that could be used to track changes in water quality accompanying hydraulic fracturing in the region in the future.

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The research in the second and third chapters of this dissertation was funded by the Environmental Defense Fund and Duke University's Nicholas School of the Environment. The research in the fourth chapter was funded by the Water Resources Research Institute. The work in the third chapter would not have been possible without the instrument generously provided free of charge by Aerodyne Research, Inc.

1

Introduction

1.1 Motivation

Energy use is a large and growing driver of global change. In particular, the amount of natural gas used to generate energy, especially in the United States, has increased rapidly as a result of widespread hydraulic fracturing. The amount of electricity generated from natural gas in the United States nearly doubled between 1993 and 2011 and is projected to be nearly equal to that generated from coal by 2040 (Office of Integrated Analysis and Forecasting, 2009).

Increasing use of natural gas poses both opportunities and risks. As a fuel source to generate electricity, natural gas emits less carbon dioxide (CO_2) per unit of energy produced than does burning coal (Alvarez et al., 2012). Moreover, burning coal releases mercury and coal ash, thus contributing to health-related externalities, whereas burning natural gas does not (National Research Council, 2010).

However, natural gas use and extraction also carries risks. *In this thesis, I seek to address two critical uncertainties in the assessment of hydraulic fracturing and natural gas as a source of energy: 1) methane emissions to the atmosphere (chapters 2 and 3) and potential contamination of groundwater supplies (chapter 4).*

1.2 Atmospheric methane emissions

Human activities have significant impact on the global methane (CH_4) budget and produce approximately half of the CH_4 emitted to the atmosphere (Neef et al., 2010). Humans have greatly enhanced some existing sources of CH_4 to the atmosphere, such as by increasing ruminant animal populations for livestock. CH_4 from geologic formations enters the atmosphere through surface seeps, but humans have more than doubled the rate of thermogenic CH_4 emissions through fossil fuel extraction and use (Kirschke et al., 2013). In other cases, such as CH_4 emissions from wetlands, it is unclear what the cumulative impact from humans has been, either directly through the creation and destruction of wetlands or indirectly through climate disruptions (Bridgham et al., 2013). Improving our understanding of the CH_4 budget could lead to more effective targeted emissions reductions strategies, insights into biogeochemical CH_4 production and cycling, and more accurate predictions for future climate feedbacks.

Climate change further compounds uncertainties in the current CH_4 budget. Climate change is causing particularly rapid warming in the Arctic, which could lead to widespread wetland formation as permafrost melts (Bridgham et al., 2013). Atmospheric CH_4 concentration has changed rapidly in the past, such as during the Younger Dryas–Preboreal transition ~11,600 years ago, in which atmospheric [CH_4] increased by ~200 ppb in about 200 years. This rapid increase was likely due to enhanced CH_4 production from wetlands (Petrenko et al., 2009). Warming in arctic regions could also release some or all of the vast amount of CH_4 stored as hydrates (Kirschke et al., 2013). While neither of these effects has been observed to date (Dlugokencky et al., 2009), it is not clear whether CH_4 hydrates may rapidly destabilize once some as-yet unknown climate threshold is passed. Even in the absence of these large non-linear responses from biogenic and non-biogenic CH_4 sources,

the current growth rate in atmospheric [CH_4] of ∼4 ppb per year (Bousquet et al., 2006) is more rapid than that observed during past major climate transitions.

It is essential to take rapid, decisive actions now to address the causes and mitigate the effects of climate change, as those costs and hardships are very likely to increase exponentially in the future (Stocker et al., 2013). Targeting CH_4 emissions is an important part of that rapid greenhouse gas reduction strategy. CH_4 is the second-most important anthropogenic greenhouse gas after carbon dioxide (CO_2), with a warming effect 84 times that of CO_2 over a 20-year time horizon (Stocker et al., 2013). CH_4 accounts for about a third of anthropogenic radiative forcing (Kirschke et al., 2013). Because of its relatively short atmospheric lifetime (∼12.4 years; Stocker et al., 2013), reducing CH_4 emissions would lead to rapid reductions in global atmospheric greenhouse gas burdens. Moreover, it is feasible with current technology, and potentially even profitable (Katzenstein et al., 2003), to reduce CH_4 emission from some of the largest anthropogenic sources, such as natural gas infrastructure and waste management.

The current rapid increase in CH_4 extraction and use due to widespread hydraulic fracturing has potential tradeoffs for global greenhouse gas emissions. Natural gas is altering energy use patterns primarily by replacing coal in electricity generation (Weber and Clavin, 2012). Burning natural gas to generate electricity produces less CO_2 per unit of energy than burning coal, and natural-gas-fired power plants are also more efficient than coal power plants (by 5% on average in the U.S.), compounding the reductions in CO_2 emissions (Hultman et al., 2011). CO_2 emissions from electricity generation in the U.S. fell by 8.76% in the U.S. between 2008 and 2009 due to increasing power generation from natural gas (Lu et al., 2012).

However, because of CH_4's high greenhouse warming potential, leaks of uncombusted CH_4 to the atmosphere from natural gas extraction, transport, and use greater than ∼3.2% of production could negate the greenhouse gas benefits rela-

tive to coal (Wigley, 2011). Measuring the leakage rate from the natural gas supply chain is complicated by the range of spatial scales and environments spanned by the system, from individual gas wells to interstate pipeline networks. It is possible that a small number of high-intensity sources are responsible for a disproportionate share of the CH_4 emissions from the energy sector (Brandt et al., 2014).

Current estimates for CH_4 emissions from the natural gas supply chain vary widely (Weber and Clavin, 2012), from ∼1% to to nearly 8% of production (Howarth et al., 2011). The U.S. Environmental Protection Agency estimates that 0.7% of annual natural gas production in the U.S. is lost to leaks in transportation infrastructure, which is almost half of the 1.5% leak rate estimated for the total natural gas supply chain (Brandt et al., 2014). Leakage from natural gas infrastructure, combined with other CH_4 sources in urban areas, such as wastewater treatment facilities and landfills, could make CH_4 emissions from urban areas 21-34% of total anthropogenic CH_4 emissions (Wunch et al., 2009).

One aim of this thesis is to reduce the uncertainty in CH_4 emissions from the natural gas supply chain. I focus particularly on CH_4 emissions from urban natural gas distribution infrastructure, which have been shown to be a potentially large component of the total loss rate from the energy sector (Phillips et al., 2013; Jackson et al., 2014). I develop a set of chemical fingerprints which can be used to identify CH_4 sources in a variety of environments, including urban areas (chapter 3). I use those fingerprints to identify the urban natural gas distribution system as the primary source of CH_4 measured at street level (chapter 3), as well as to partition the total urban CH_4 flux between biological and thermogenic sources (chapter 4). Doing so, I find that 88% (95% CI: 82–94%) of the CH_4 in the atmosphere above Boston is due to thermogenic sources (chapter 4). This research is part of the large and ongoing effort to quantify fugitive CH_4 emissions and ultimately assess the viability of natural gas as a fuel source with lower greenhouse gas impact than other fossil fuels.

1.3 Hydrologic impacts of shale gas extraction

In addition to its effect on atmospheric CH_4, there is evidence that hydraulic fracturing can significantly impact groundwater quality (Vengosh et al., 2014). Elevated levels of dissolved CH_4 have been observed in shallow drinking water near hydraulically fractured gas wells (Osborn et al., 2011a; Jackson et al., 2013). In Pennsylvania, well water samples with elevated CH_4 had δ^{13}C-CH_4 > -55‰ and also contained higher-chain hydrocarbons such as C_2H_6 and propane (C_3H_8), both strongly suggestive of a thermogenic CH_4 source and not the result of biological CH_4 production (Jackson et al., 2013). The most likely sources for the thermogenic CH_4 entering shallow groundwater supplies near natural gas wells are faulty gas well casings and cementing around casings, which allow CH_4 to flow up to the surface (Vengosh et al., 2014). Another potential avenue for CH_4 migration into groundwater following hydraulic fracturing is via connection with existing or incipient geologic fractures. However, assessing the risks associated with this pathway are complex and the resulting migration may occur at longer timescales after drilling than have thus far been possible to measure (maximum ∼10 years).

While stray gas contamination has been observed previously, groundwater contamination by other components of the drilling process remains more controversial. The mix of chemicals injected into gas wells during the hydraulic fracturing process include acids, viscosity reducers, corrosion inhibitors, biocides, and friction reducers (Vidic et al., 2013). As with geologic CH_4 migration pathways, it is possible that subsurface migration of contaminants will only become apparent over longer timescales more relevant to groundwater flow (Vengosh et al., 2014). There is evidence that, in Pennsylvania's Marcellus shale at least, connective pathways exist between saline fluids from shale formations and shallow aquifers (Warner et al., 2012). While it is likely that these pathways enhance the risk of shallow groundwater ac-

companying hydraulic fracturing, the details of this relationship remain unknown.

Subsurface migration is not the only pathway by which hydraulic fracturing can potentially impact water supplies. About 10–40% of the volume of fluid injected into a hydraulically fractured well is returned to the surface over the lifetime of that well (Gregory et al., 2011). This waste water, called produced water or flowback water depending on how long after injection it returns to the surface, can contain high concentrations of salts and toxic elements such as barium, strontium, and radium. Produced water and flowback water can also contain organic compounds, such as benzene and toluene (e.g. BTEX compounds), resulting from the chemicals introduced in the drilling process and their breakdown products (Kassotis et al., 2013). These waste fluids are sometimes stored in constructed ponds, which can lead to groundwater and surface water contamination when ponds leak or are breached, as was documented, for example, in Pavilion, WY, where elevated BTEX concentrations were observed in groundwater near waste ponds associated with hydraulically fractured wells (DiGuilio et al., 2011). Insufficient treatment of waste water can also lead to surface water contamination at disposal sites. Warner et al. (2013b) found elevated levels of salinity, barium, strontium, radium isotopes, and organic compounds such as benzene and toluene in discharges from flowback water and produced water treatment facilities in Pennsylvania. Bromide concentrations were elevated more than ten times background approximately 2 km downstream (Warner et al., 2013b).

Assessing the risks that hydraulic fracturing could pose to water supplies in a region requires a detailed understanding of the chemical composition of the groundwater in the region, including concentrations of dissolved hydrocarbons as well as major ions, trace elements, and organic compounds. Knowledge of the shallow groundwater quality is necessary to assess changes potentially induced by hydraulic fracturing in the area, and the chemical signature of deep groundwater could influence the wastewater produced by gas wells. As such, comparing water quality data before

and after hydraulic fracturing has occurred can provide insight into potential effects on groundwater resources.

However, lack of pre-drilling background data for groundwater composition, especially CH_4 concentration, has complicated efforts to evaluate the hydrogeologic impact of hydraulic fracturing (Davies, 2011; Saba and Orzechowski, 2011; Schon, 2011; Osborn et al., 2011b). CH_4 has not been routinely measured in surveys of groundwater quality in the past, and thus existing CH_4 data in many parts of the United States are sparse. For example, the U.S. Geological Survey's (USGS) National Water Information System (database) includes no measurements of dissolved CH_4 in groundwater anywhere in Pennsylvania, few in the areas of New York above the Marcellus formation, and none in the Deep River Basin of North Carolina (Fig. 1.1). Better knowledge of the CH_4 concentration in groundwater preceding hydraulic fracturing would allow for comparisons of groundwater quality before and after drilling.

In chapter 4 of this thesis, I provide groundwater quality data that could be useful in assessing the hydrogeologic impacts of shale gas drilling, particularly in central North Carolina. This area is unique in that it has no pre-existing oil or gas drilling. While this study focuses on water chemistry, particularly dissolved CH_4, the two appendices to this thesis provide a broader exploration of the potential environmental impacts from hydraulic fracturing in North Carolina.

1.4 Summary

In this thesis, I seek to address uncertainties that currently prevent a full assessment of the risks associated with natural gas extraction and use. In chapters 2 and 3, I work towards quantifying CH_4 emissions from the natural gas distribution system in urban Boston, MA. Reducing uncertainty in the loss rate of natural gas from distribution systems is essential to assessing the climate benefits of natural gas as a fuel source relative to coal and other fuels. A better understanding of natural gas

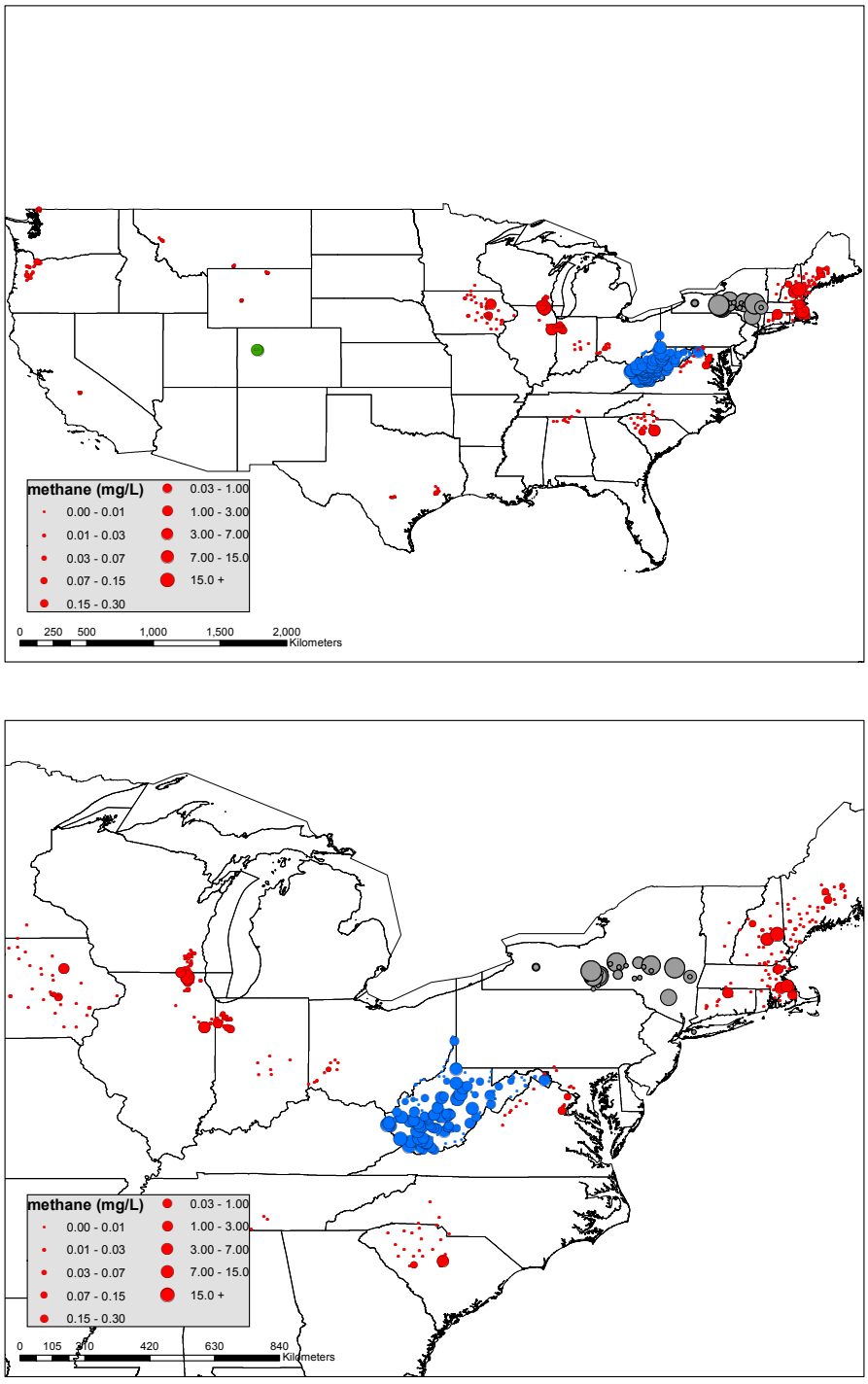

FIGURE 1.1: CH_4 in drinking water, drawn from USGS data. Color represents data source: blue: White and Mathes, 2006; red: Hinkle et al., 2010; green: McMahon et al., 2011; grey: National Water Information System for New York, Pennsylvania, and central North Carolina.

emissions could lead to relatively easy opportunities for short-term greenhouse gas reductions. In chapter 4, I provide what is, to my knowledge, the first comprehensive survey of the water quality in NC's Deep River Basin, an area that could have hydraulic fracturing for natural gas in the future. This work provides a baseline that can be used to assess future changes in groundwater quality if drilling occurs. Our water quality data set also provides some preliminary insight into the potential risks associated with hydraulic fracturing in North Carolina and contributes to the ongoing effort to assess the hydrologic risks from hydraulic fracturing in diverse environments.

2

Urban methane source identification using carbon isotopes and ethane

2.1 Abstract

Leaks from natural gas infrastructure are the largest anthropogenic source of methane in the United States and the second largest globally. To better identify leaks associated with natural gas infrastructure, we measured the δ^{13}C isotopic signature of methane and methane-to-ethane ratio of multiple urban sources in Boston, MA, including wetlands, landfills, and the commercial natural gas supply. Using pipeline databases, we also created a time series of the methane (CH_4) and ethane (C_2H_6) content of the natural gas flowing into the Boston area from October, 2012 to February, 2014. Comparing these δ^{13}C-CH_4 and [CH_4] / [C_2H_6] values to those of over 150 flask samples taken from CH_4 point sources in Boston, we found natural gas infrastructure to be the major source of CH_4 measured at ground-level in the city. The δ^{13}C-CH_4 and [CH_4] / [C_2H_6] of flask samples collected from street manholes and catch basins was statistically indistinguishable from that of pipeline natural gas samples (δ^{13}C-CH_4: $p > 0.99$, $n = 109$; [CH_4] / [C_2H_6]: $p > 0.99$, $n = 28$). We used

a mobile cavity-ringdown spectrometer to further investigate potential CH_4 emissions from different urban CH_4 sources, including gasoline (n = 13) and compressed natural gas (CNG, n=2) filling stations. Based on field sampling, gasoline filling stations are not likely to be a significant source of atmospheric CH_4 in this urban area, as all gasoline stations sampled had [CH_4] at or below background [CH_4]. The two CNG filling stations we measured, however, had significantly elevated [CH_4] in the immediate vicinity (∼5 m) during all of our surveys. Finding and fixing leaks in CH_4 infrastructure could help save money, improve urban air quality, and reduce greenhouse gas emissions.

2.2 Introduction

Methane (CH_4) is the second most important anthropogenic greenhouse gas globally after carbon dioxide and is responsible for roughly 20% of the anthropogenic radiative forcing (Butler, 2011). The atmospheric CH_4 concentration has increased more than 2.5 fold since pre-industrial times to >1800 ppb today (Skeie et al., 2011). CH_4 is 28 times more potent as a greenhouse gas, molecule for molecule, than CO_2 over a 100-year time horizon, and 84 times more potent over a 20-year time horizon (Stocker et al., 2013). However, reductions in CH_4 emissions could have a large and immediate impact on the atmospheric greenhouse gas burden, as CH_4 has a shorter atmospheric lifetime, ∼12.4 years, than CO_2 (Dlugokencky et al., 2011). CH_4 is also a precursor for ground level ozone, and ozone resulting from elevated concentration of CH_4 and other hydrocarbons can negatively impact human health, particularly in urban areas (West et al., 2006).

Anthropogenic CH_4 sources account for approximately 335 Tg, or 60%, of the global total 580 Tg of CH_4 emitted annually (Kirschke et al., 2013). The largest anthropogenic CH_4 source in the Untied States is natural gas production and distribution, which accounts for ∼220 Tg CO_2 equivalent (CO_2 Eq.) of the 686 Tg CO_2

Eq. of CH_4 emitted annually in the US, followed by emissions from livestock (approximately 140 Tg / yr CO_2 Eq.) and landfills (around 118 Tg / yr CO_2 Eq.) (U.S. Environmental Protection Agency, 2011). However, there are significant uncertainties remaining in the global CH_4 budget (Kirschke et al., 2013). In particular, leakage rates from urban natural gas infrastructure could represent a large and relatively poorly constrained source of CH_4 emissions, with possibly 0.7 % of commercial natural gas production in the United States lost to leakage in transmission and distribution infrastructure (Brandt et al., 2014). The resulting CH_4 enhancement in urban areas could be important globally, with possibly 21–34 % of anthropogenic CH_4 emissions coming from urban areas (Wunch et al., 2009). Here, we refine isotopic and ethane (C_2H_6) signatures for potential CH_4 sources, focusing specifically on CH_4 emissions from urban areas. These identification techniques could help constrain the overall CH_4 budget and improve the understanding of CH_4 emissions from urban areas (Brandt et al., 2014; Wunch et al., 2009).

There are three broad categories of CH_4 sources globally: biogenic, thermogenic, and pyrogenic. Biogenic CH_4 is produced by methanogenic bacteria in anaerobic environments that include wetlands, landfills, wastewater treatment facilities, and enteric fermentation in livestock. Thermogenic CH_4 is produced from the conversion of organic matter into fossil fuel over geologic timescales under high temperature and pressure, and can be released from sources that include the extraction and burning of fossil fuels and natural geologic seeps. Pyrogenic CH_4 results from the incomplete combustion of biomass, primarily during wildfires. Each of these CH_4 sources have distinct $\delta^{13}C$ isotopic ranges (all C isotopic ratios in standard delta notation, relative to Vienna Pee Dee Belemnite): -70 to -55 ‰ for biogenic sources, -55 to -25 ‰ for thermogenic sources, and >-25 ‰ for pyrogenic sources (Whiticar, 1999; Kirschke et al., 2013). These distinctive isotopic ranges have been used to identify and differentiate CH_4 sources, particularly those associated with anthropogenic ac-

tivities (Kai et al., 2011; Conrad, 2005; Townsend-Small et al., 2012). Higher-chain hydrocarbons such as C_2H_6 and propane can co-occur with CH_4 formed thermogenically, but biogenic CH_4 sources typically produce no hydrocarbons other than CH_4. Thus, the co-occurrence of C_2H_6 with CH_4 can be used to identify thermogenic CH_4 sources (Wennberg et al., 2012; Jenden et al., 1988).

Work by Phillips et al. (2013) and Jackson et al. (2014) has demonstrated the large number of CH_4 plumes on roadways in urban areas. Surveying CH_4 concentration on the streets of Boston, MA, USA, Phillips et al. (2013) found 3356 individual CH_4 spikes where $[CH_4]$ measured on roadways exceeded 2.5 ppm, which is higher than the natural background $[CH_4]$ of 1.8–2.0 ppm. CH_4 spikes had concentrations 15 and 45 times higher than background in Boston and Washington, DC, respectively. In both cases, isotopic evidence and elevated ethane levels suggested fossil-fuel sources were responsible for the CH_4 plumes, most likely from the natural gas infrastructure.

In this paper, we examine the $\delta^{13}C$ fingerprint of urban CH_4 sources in Boston, MA with a larger number of CH_4 point-source samples ($\delta^{13}C$-CH_4, n = 176; $[CH_4]$ / $[C_2H_6]$, n = 43) and a diverse array of biogenic CH_4 sources. On a subset of our samples, we measured C_2H_6 concentration, which provides further differentiation between biogenic and thermogenic CH_4 sources. We compared the C_2H_6 concentration of our point-source samples to a time series of $[CH_4]$ and $[C_2H_6]$ of natural gas in interstate pipelines that supply the Boston metro area. We also evaluated to what extent point sources other than the natural gas distribution network could contribute to thermogenic CH_4 emissions in the Boston area by measuring CH_4 concentration near liquified natural gas bus depots, gasoline filling stations, and other hydrocarbon infrastructure.

2.3 Methods

2.3.1 Sample collection

We collected samples from a variety of potential CH_4 point sources in the Boston area: natural gas infrastructure, wetlands, landfills, and the only sewage treatment facility in the area, the Deer Island sewage treatment plant (Fig. 2.1), to analyze for gas concentration and isotopic composition. We also randomly sampled 109 street leaks that had CH_4 concentrations >5 ppm as measured by Phillips et al. (2013), 2.5 times background [CH_4] in the city air, to examine the source. All samples were collected between September, 2011 and August, 2013.

Samples measured for δ^{13}C-CH_4 were collected in 1-L Tedlar sampling bags (Environmental Supply Co., Durham, NC, USA), following the protocol in Phillips et al. (2013). Samples analyzed for higher chain hydrocarbons were collected in 150-ml stainless steel cylinders with valves on both ends (Swagelok, Solon, OH, USA). During sampling, one end of the sampling vessel was connected to 0.5 m of Synflex 1300 metal/plastic composite tubing (Eaton Corporation, Dublin, Ireland), which was used to collect samples from beneath manhole covers, within storm drains, and from landfill vent pipe outlets. Gas was collected in the sampling vessel by aspirating sample gas through the vessel using a hand pump connected to the sampling apparatus upstream of the sampling vessel. After at least three times the volume of the sampling canister and tubing (approximately 500 ml) had passed through the system during aspiration, both valves of the sampling vessel were closed simultaneously to trap the sample gas after flushing the sampling apparatus (approximately 500 ml) with at least three volumes of sample gas. The hand pump and sampling tubing was flushed with minimum 1 L of ambient air between sample collections, which is much greater than the combined volume of the tubing (2.2 mm inner diameter, 0.015 L per m of tubing) and pump (approximately 0.01 L).

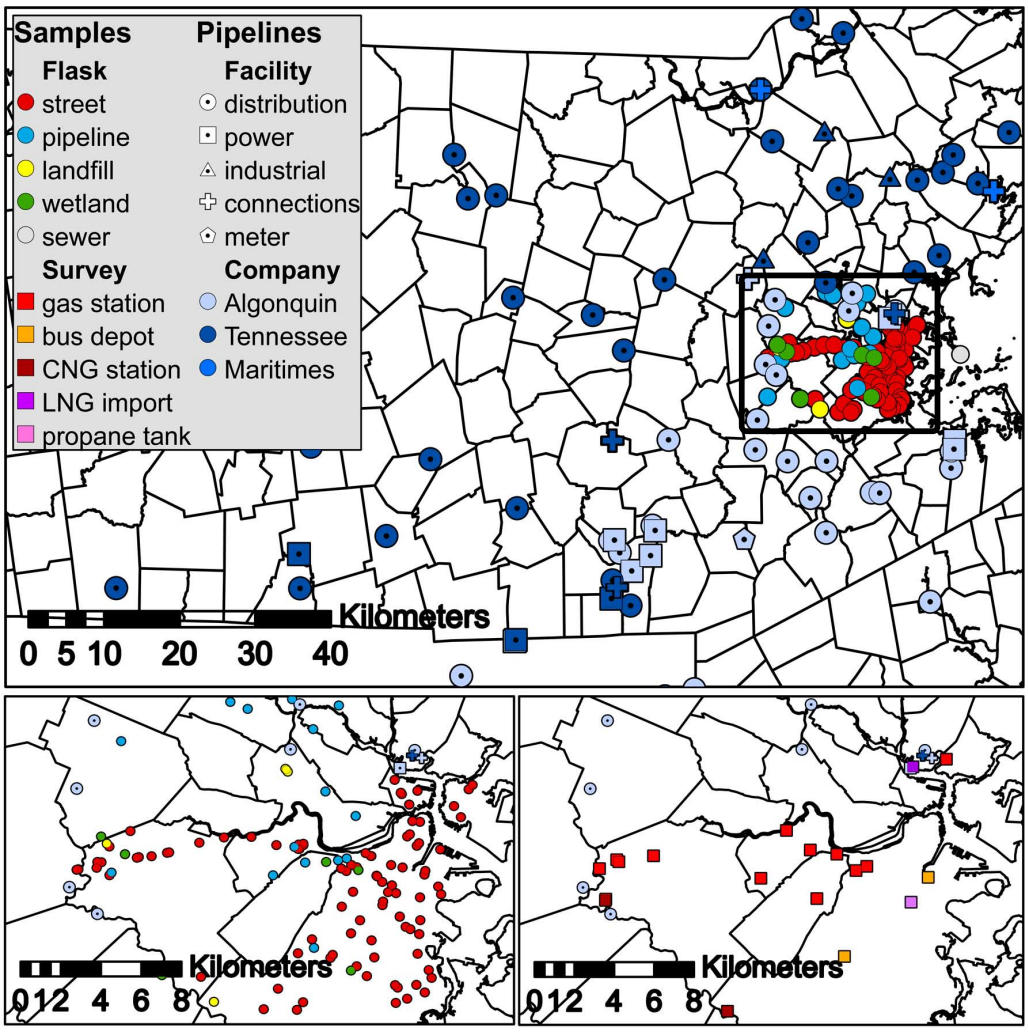

FIGURE 2.1: Locations of point source flask samples, industrial point source surveys, and pipeline facilities. Point source sampling locations are indicated by circles, separated by type of sample: wetland (green), landfill (yellow), pipeline (blue), and street (red). Industrial point sources surveyed with the mobile [CH_4] instrument are shown as squares in bottom right panel, with color representing source type: gasoline filling stations (red), bus depots (orange), CNG filling stations (dark red), LNG import facility (purple), industrial propane tank (pink). Facilities on the three interstate pipelines in the Boston area are also shown: Algonquin in light blue, Maritimes and Northeast in blue, and Tennessee in dark blue. Type of pipeline facilities is indicated by shape: distribution stations (circle), where the interstate lines connect to local distribution networks; power plants (square); industrial facilities (triangle), including manufacturing and military facilities; metering stations (pentagon) where natural gas composition is recorded; and interconnections (cross) between interstate pipelines. The black rectangle around the Boston metro area in the top panel is the extent of the zoomed view in the bottom two panels.

Wetland samples for δ^{13}C-CH_4 and hydrocarbon quantification were collected using a plastic chamber (0.25 m^2) placed over shallow sediments (~0–5 cm water depth). The chamber was left on the water surface for a minimum of 2 minutes before the sample was collected. The chamber was connected to a stainless steel sampling vessel via a maximum of 3 m of Synflex tubing, and sample gas was collected via aspiration with a hand pump.

Landfill sampling procedures varied by site. As there are no active landfills in the Boston area but several capped landfills, we sampled capped landfills as sources of CH_4 and, less likely, C_2H_6 to city air. The Newton compost site, a capped landfill in Newton, MA, was sampled directly from gas vent pipe on the top of the facility. We collected six additional samples from capped landfills that have been converted into parks (Millennium Park and Danehy Park). Samples from these locations were collected from infrastructure that penetrates the surface of the park, including storm drains and structure foundations.

Sewage samples were collected in glass volatile organic assessment (VOA) vials from the anaerobic sewage digesters at the Deer Island wastewater treatment facility. This facility treats all of the wastewater from the Boston metro area and is the only wastewater treatment facility in the area.

Natural gas samples taken directly from pipelines and end-use points (e.g., stoves and burners) were collected from private homes, businesses, and universities. A number of samples (n = 14) were collected from domestic and commercial natural gas supplies connected to the low pressure natural gas distribution system within 1 km of intersections between the high pressure interstate pipelines and the low pressure distribution system. The rest of the pipeline samples (n = 29) were collected from natural gas supplies in laboratory hoods at universities. Building managers at Boston University confirmed that these university building gas supplies draw directly from municipal gas lines. Laboratory gas taps were purged for a minimum of 5 minutes

before samples were collected to draw fresh gas directly from the municipal system. Previous tests that we performed on the fume hood gas supplies at Boston University showed that the δ^{13}C signature of pipeline gas samples collected every 30 seconds from a university gas tap not used for ~6 months stabilized within 5 minutes of purging.

2.3.2 $\delta^{13}C$-CH_4 analysis

δ^{13}C of CH_4 was analyzed using a Picarro G2112i Cavity Ring-Down Spectrometer (Crosson, 2008). The analysis methods follow Phillips et al. (2013). Briefly, the instrument was calibrated monthly using isotopic standards from Isometric Instruments (Victoria, BC, Canada) and checked daily to ensure analyzer output was within 1 ‰ of a tank of CH_4 with δ^{13}C-CH_4 measured by a private lab (Isotech Labs, IL). Cross-comparisons have shown this method to be in good agreement ($R^2 = 0.95$) with δ^{13}C-CH_4 analysis by Isotech Labs (Warner et al., 2013a; Jackson et al., 2013).

2.3.3 Higher chain hydrocarbon quantification

Alkane concentration was measured using an Agilent 7890A GC equipped with a flame ionization detector (FID) and an HP-PLOT/Q column. A standard curve was generated each day using alkane standards ranging in concentration from 10 ppm to 106 ppm, provided by Airgas (Radnor, PA, USA), Air Liquide (Paris, France) (see supplemental information). Samples were injected via gas-tight syringe through a 500-ml sample loop, from which the sample was then pushed onto a stainless steel trap (0.64 cm outer diameter and about 30 cm in length) packed with Porosil glass beads (Dupont, Wilmington, DE, USA) cooled to liquid-nitrogen temperature. The trap was rapidly heated to approximately 100°C to desorb the compounds and transfer them comprehensively to the GC column, where compounds were separated via the following program: 60°C to 100°C at 8°C min^{-1}, 10°C min^{-1} ramp to 200°C,

0 min hold.

Dissolved hydrocarbons in sewage digester samples were extracted by sparging with He. Sewage samples were collected in 40-ml VOA vials by staff at the Deer Island wastewater treatment facility from the facility's anaerobic CH_4 digesters. For each water sample analysis, 5 mL was withdrawn from the VOA vial and manually injected with a glass micro-mate syringe (Cadence Science Inc., RI, USA) through a 10-micron filter into a 5-mL Tekmar glass sparger on a Teledyne Tekmar Stratum Purge and Trap (Mason, OH, USA). The sample was purged for 4 minutes with 40 mL/min of purified He (Agilent Big Universal Trap Superior Helium Purifier RMSH2) and dry purged for 1 min at 40 °C and 100 mL/min. The sample was then transferred onto the Agilent 7890A GC system described above.

A dissolved CH_4 and C_2H_6 standard was created by bubbling high-purity CH_4 and C_2H_6 (Air Liquide) through 30 ml of deionized water in a 40-ml VOA vial for 10 minutes. The standard was then left for 10 minutes to equilibrate, after which time the standard was assumed to be at saturation with respect to CH_4 and C_2H_6 (25.5 mg/L for CH_4 and 34.0 mg/L for C_2H_6 at 25 °C). Aliquots of 1 to 5 ml of the gas-saturated standard were taken and diluted with deionized water to a total volume of 5 ml for each aliquot. Each of the resulting 5 dilutions was then injected onto the Teledyne Tekmar Stratum Purge and Trap and analyzed as above to create a standard curve.

All of the $[C_2H_6]$ measurements of our point-source samples except for one wetland sample had $[C_2H_6]$>100 ppt, at least two orders of magnitude above $[C_2H_6]$ background (∼1.2 ppt Simpson et al. 2012). Thus, we do not believe that our $[CH_4]/[C_2H_6]$ measurements are sensitive to ambient $[C_2H_6]$.

We constructed a time series of $[CH_4]$ and $[C_2H_6]$ for the pipeline gas entering the local distribution system in the Boston area to compare to the concentrations of the same gases in in the environment, including street leaks. The low-pressure natural gas

distribution system in Boston is tightly connected to the interstate pipeline network, and we examined all of the natural gas facilities on interstate pipelines within a 90-km radius of Boston to create an aggregated [CH_4] and [C_2H_6] signature.

Pipeline natural gas composition (i.e., [CH_4] and [C_2H_6]), capacity, and flow data are posted online by interstate pipeline management companies in compliance with US Federal Energy Regulatory Commission regulations. The higher chain hydrocarbon composition of natural gas influences the heating value of the gas, which is regulated. Natural gas pipeline capacity refers to the amount of gas that is scheduled to be delivered each day to each of the facilities located along the natural gas pipeline. According to company documentation, gas quality measurements follow the American Standards Testing and Materials method D-1945 and are measured using a variety of instruments designed specifically for natural gas analysis: Instromet Encal 2000 (Silvolde, Netherlands); ABB NCG 8206 (Bartlesville, OK, USA); and Ametek Chandler 2920 (Pittsburgh, PA, USA).

Three interstate gas pipelines enter our study area: the Algonquin pipeline (Spectra Energy, Houston, TX, USA), the Tennessee pipeline (Kinder Morgan, Houston, TX, USA), and the Maritimes and Northeast pipeline (Spectra Energy, Houston, TX, USA). The Algonquin pipeline originates in Lambertville, NJ, travels through northern NJ, southern NY, Connecticut and northern Rhode Island, and terminates near Boston, MA. In Beverly, MA, the Algonquin pipeline junctions with the Maritimes and Northeast pipeline, which continues north into New Hampshire and Maine. The Tennessee gas pipeline is an extensive network that connects areas from the Gulf of Mexico up through the Mississippi River Basin, northern Pennsylvania, and southern New York before servicing the Boston area and southern New Hampshire. The Algonquin and Tennessee pipelines are interconnected and exchange natural gas at five points within our study area (Fig. 2.1). The Maritimes and Northeast pipeline has only one interconnection with the low pressure natural gas distribution system

in the study area, located in southern New Hampshire, compared with more than 20 for each of the Algonquin and Tennessee pipelines.

We located all intersections between the interstate pipeline system and the lower pressure local distribution system in our study area. These distribution stations are the sources of the gas used domestically in the Boston area and were used to create pipeline time series of natural gas flow in this study. While gas quantity data is available for all stations, $[CH_4]$ and $[C_2H_6]$ data are available for a subset of natural gas distribution facilities (three facilities for each of the Algonquin and Tennessee pipelines in the study area). We used $[CH_4]$ and $[C_2H_6]$ data from the facility on each pipeline geographically closest to Boston, MA as most representative of the hydrocarbon signature likely to be present in the city's natural gas distribution system. For the Algonquin pipeline, we used data from Everett, MA and for the Tennessee pipeline, we used a combination of data from Malden (approximately 95% of our time series) and Revere, MA (time periods for which data from Malden was not available). Facility locations were identified using the National Pipeline Mapping System and cross-referenced using satellite images from Google Earth. Where possible, facilities were further cross-referenced using Google Street View images to confirm both the location and the facility classification as distribution stations (e.g. not power plants, industrial facilities, etc.).

The amount of gas flowing through distribution stations was similar between the Algonquin and Tennessee pipelines and showed a seasonal pattern consistent with a cold Northern Hemisphere climate where natural gas is used for residential heating (Fig. 2.4, top). This flow through distribution stations, which represents the natural gas delivered from the interstate pipeline network to the local low-pressure distribution system, rises sharply in mid-October and remains high until the end of May, inversely tracking the temperature pattern in the Boston area. The ratio of the amount of gas flow in the Algonquin pipeline relative to the sum of the total

varied between ∼0.50 and ∼0.65, with one brief exception in the early fall of 2012, and showed no clear seasonal pattern.

2.3.4 Point-source survey

We tested for CH_4 emissions from potential industrial sources of CH_4 by surveying CH_4 concentration with a Picarro G2301 cavity ring-down spectrometer (CRDS) mounted in a vehicle, following the methods in Phillips et al. (2013) and Jackson et al. (2014). Spectrometer and mobile GPS data were recorded every 1.1 s, and air was sampled through a 3.0 um Zefluor filter and Teflon tubing. The instrument inlet was placed ∼30 cm above road surfaces while in motion, and ∼150 cm above road surfaces while conducting stationary sampling of industrial facilities.

We tested for CH_4 emissions from gasoline filling stations (n = 13), compressed natural gas filling stations (n = 2), compressed natural gas bus depots (n = 2), an industrial liquified propane gas storage tank, and the liquified natural gas (LNG) import terminal in Everett, MA, collectively referred to as potential industrial sources of CH_4. Each gasoline filling station that we surveyed was tested once. All other potential industrial sources were surveyed three times: December 2012, March 2013, and August 2013. At each location, we measured methane concentration above, adjacent to, or downwind of the facility (depending on the source type) for a minimum of five minutes. During this sampling time, the CRDS instrument was stationary and the instrument inlet was elevated to ∼150 cm. We compared these "signal" measurements to data from other time periods collected while driving that represent local background [CH_4]. For gasoline filling stations, CNG filling stations, and the LPG storage tank, we considered background data to be [CH_4] data measured while driving that met three criteria. First, the background data were collected within five minutes of arriving at or departing the potential source. Second, the background data were collected within 1 km of the potential source. Third, background data

could not contain "leaks" as defined by Phillips et al. (2013) in which [CH_4] exceeds 2.5 ppm. Any peaks in which measured [CH_4] exceeded 2.5 ppm were removed from the background data.

For each potential CH_4 source, we fit both the CH_4 concentration data from the signal and background time periods with autoregressive integrated moving average (ARIMA) models. We then compared the parameters of these fits using the Chow test of statistical significance to determine if the signal data had significantly higher [CH_4] than the background time period. The Chow test determines whether the coefficients of linear models for two datasets are statistically different by comparing the parameters for each fit with the parameters that result from fitting the combined dataset (Chow, 1960). We computed ARIMA models with one integrated term and no autoregressive or averaging terms, (i.e. (p, d, q) = (0, 1, 0)), thus estimating only the mean [CH_4] for each data set and not the temporal characteristics.

2.4 Results and Discussion

2.4.1 Point source sampling

The δ^{13}C values of biogenic CH_4 sources ranged from -64.9 ‰ to -47.0 ‰, with a group mean for all biogenic methane sources of -57.0 ‰ (Fig. 2.2). The δ^{13}C values of our pipeline samples had a clear thermogenic signature on average and ranged from -57.0 to -30.1 ‰ (mean: -39.5 ‰, sd: 5.83). The δ^{13}C values of our street samples (mean: -39.8 ‰, sd: 7.8) were similar to those of our pipeline samples, although with larger variance (Fig. 2.2, left panel). The street samples that we measured were indistinguishable from our pipeline samples ($p > 0.99$) and distinguishable from our biogenic samples ($p < 0.001$, with Bonferroni post-hoc adjustment for multiple comparisons). The δ^{13}C values of the aggregated biogenic and pipeline CH_4 sources differed by almost 20 ‰ ($p < 0.001$). Because these groups were clearly distinguishable, we used the group means for our biogenic (-57 ‰, sd: 4.2) samples

to compare to our street samples.

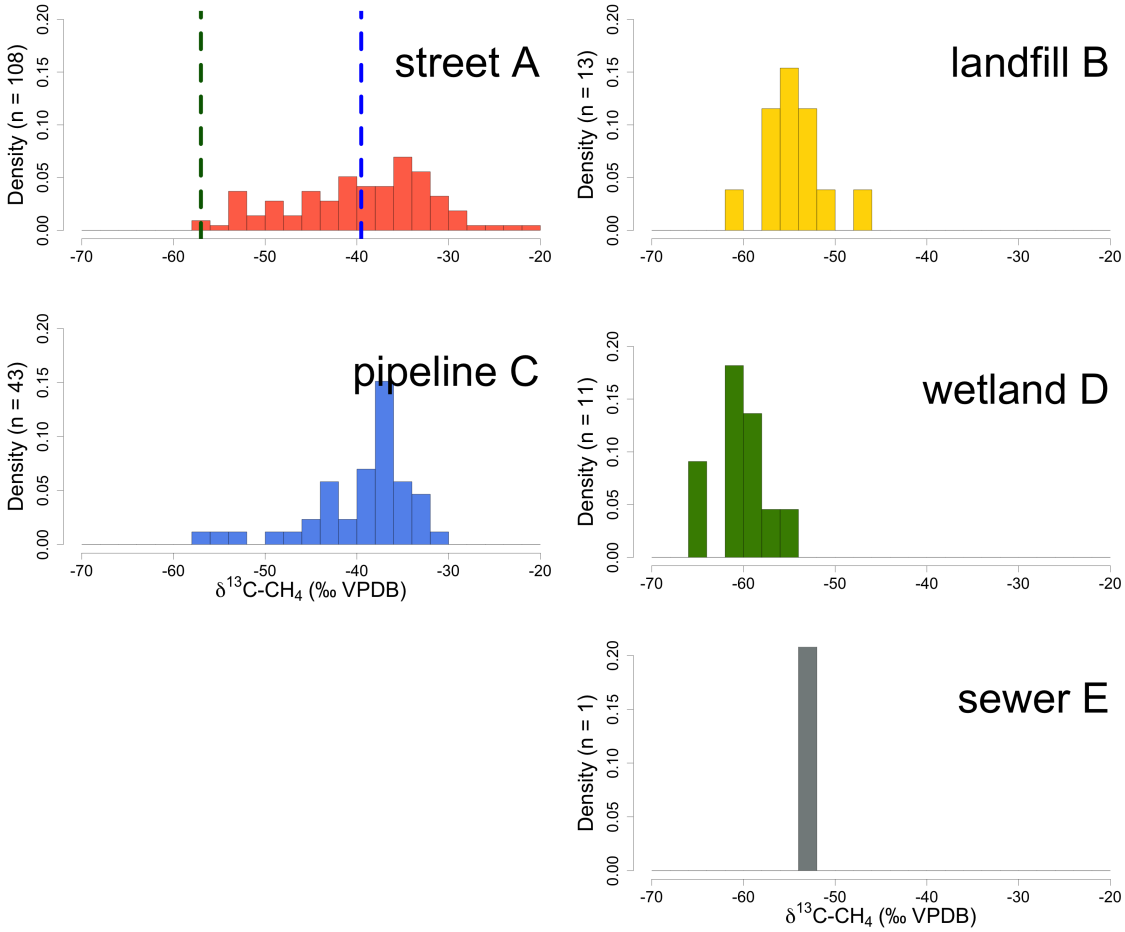

FIGURE 2.2: Histograms of δ^{13}C-CH_4 of point source samples, with mean δ^{13}C-CH_4 of all biogenic (panel B: landfill; D: wetland; and E: sewer) samples (green dotted line, panel A) and mean δ^{13}C-CH_4 of all pipeline samples (dotted blue line, panel A). Mean δ^{13}C-CH_4 of street samples is indistinguishable from that of pipeline samples ($p > 0.99$), but significantly different than the mean δ^{13}C-CH_4 of biogenic samples ($p < 0.001$), suggesting that methane emissions observed on streets are primarily due to leaks in the underlying natural gas infrastructure.

C_2H_6 concentrations in our samples further supported the conclusion that street samples represented pipeline natural gas (Fig. 2.3). The [C_2H_6] values in the pipeline gas flask samples ranged from ~1.3 to 3.0 percent C_2H_6, resulting in a ratio of [CH_4] / [C_2H_6] from 33.0 to 73.8 (mean = 42.8), similar to that observed by Wennberg et al. (2012) in Los Angeles, CA, USA. Our street samples were similar in [CH_4] /

$[C_2H_6]$ to our pipeline samples, with street samples $[CH_4]$ / $[C_2H_6]$ ranging from 19.5 to 121.2, with a mean of 46.7. The mean $[CH_4]$ / $[C_2H_6]$ value for street samples was statistically indistinguishable from that of pipeline samples ($p > 0.99$). In contrast, the ratio of $[CH_4]$ / $[C_2H_6]$ in biogenic samples was >200 for all samples, and for most samples was much higher (Fig. 2.3). The wetland sample with the lowest $[CH_4]$ / $[C_2H_6]$ value (211.9) collected at the Back Bay Fen, in downtown Boston was still twice as high as any of our street samples.

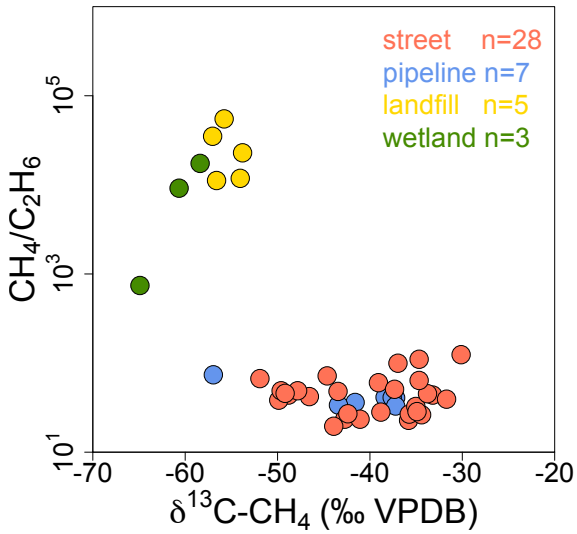

FIGURE 2.3: Ratio of $[CH_4]$ to $[C_2H_6]$ vs. δ^{13}C-CH_4 for point source flask samples. The mean $[CH_4]$ / $[C_2H_6]$ ratio for street samples is not significantly different than that of pipeline samples, but is distinct from the means of wetland and landfill samples (p ¡ 0.001). The $[CH_4]$ / $[C_2H_6]$ ratio provides further evidence that the methane observed in street samples is a result of natural gas infrastructure leaks.

We found that the δ^{13}C signatures of wetlands and landfills were distinct ($p < 0.001$), with wetland samples having a lighter, more depleted signature and less variance (mean: -60.2 ‰, sd: 2.9) than landfill samples (mean: -54.6 ‰, sd: 3.4). The relative less depleted mean δ^{13}C signatures of our landfill samples relative to our wetland samples is consistent with CH_4 production primarily by acetate fermentation in landfills and, in wetlands, by a mixture of acetate fermentation and CO_2 reduction,

which results in greater isotopic fractionation (Whiticar et al., 1986). The δ^{13}C values of our landfill samples matched those found in other cities (-55.4‰, Zinchenko et al. (2002); Phillips et al. (2013)) and falls within the large range of values for δ^{13}C-CH_4 of landfill gas presented in Bergamaschi et al. (1998). Although our samples were drawn from both gas collection systems and soil gas from capped landfills, we found δ^{13}C values from these two types of landfill samples to be statistically indistinguishable ($P = 0.90$). The δ^{13}C values of our wetland samples (mean: -60.2 ‰, sd: 2.9) are slightly higher on average than that measured at another wetland (-64.5‰ $\pm$ 0.8), in New England, USA (Santoni et al., 2012).

Comparison of $[CH_4]$ / $[C_2H_6]$ to δ^{13}C of street samples suggests that the variation observed in δ^{13}C of pipeline and street samples is not the result of mixing between thermogenic and biogenic CH_4 sources. Biogenic methane tends to have δ^{13}C of <-55 ‰ (Whiticar, 1999), and also little or no associated C_2H_6. Mixing between biogenic and thermogenic CH_4 would tend to create a negative correlation between $[CH_4]$ / $[C_2H_6]$ and δ^{13}C, as adding biogenic CH_4 to a purely thermogenic pool of CH_4 would simultaneously make the δ^{13}C value of the pool more depleted and increase the $[CH_4]$ / $[C_2H_6]$ ratio. We do not observe this pattern in our street or pipeline samples (Fig. 2.3), with δ^{13}C of street and pipeline samples showing no correlation with $[CH_4]$ / $[C_2H_6]$ ratio. This lack of correlation suggests that variation in δ^{13}C values of street and pipeline samples is more likely due to a variation in the δ^{13}C signature of the pipeline source gas than to mixing with biogenic methane sources.

Some of the variation in the δ^{13}C values of our street samples could be caused by the variation in the δ^{13}C of the pipeline gas that is the most likely source for these emissions. Mixing between pipeline gas and biogenic CH_4, possibly from the sewer system, could result in some of the depleted δ^{13}C values observed, although this seems unlikely based on the ethane concentrations that we measured in our

street samples. Soil oxidation could fractionate the $\delta^{13}C$ of CH_4 in natural gas leaked in the subsurface. However, soil fractionation would tend to shift the $\delta^{13}C$ of CH_4 passing through soil to enriched values as ^{12}C is preferentially oxidized by methanotrophs (Mahieu et al., 2006). Diffusive transport could also affect the $\delta^{13}C$-CH_4, preferentially retarding the movement of ^{13}C, although the fractionating effect of diffusive transport over short distances is likely minimal (Zhang and Krooss, 2001; Prinzhofer and Pernaton, 1997).

The $\delta^{13}C$ of pipeline gas was more enriched during spring/summer months (April to September mean: -37.7 ‰) than during fall/winter months (October to March mean: -44.2 ‰). This significant seasonal difference ($p < 0.01$) is likely due to the influx of LNG into the Boston natural gas system in the winter. Much of the LNG imported to the US comes from Trinidad and Tobago and has a depleted $\delta^{13}C$ signature around -50 ‰, more similar to that of biological methane sources (Jaramillo et al., 2007). In contrast, the seasonal trend in the $\delta^{13}C$ of the pipeline samples was not observed in the street samples. Borjesson et al. (2001) observed no seasonal variation in $\delta^{13}C$ values for landfill CH_4 emissions, and our landfill samples also show no clear seasonal trend (Fig. 2.5, top panel). Likewise, the $\delta^{13}C$ values of our wetland samples exhibited no clear seasonal pattern, suggesting that the fractionation factor associated with wetland CH_4 formation is relatively unaffected by temperature or biological productivity.

2.4.2 Pipeline natural gas composition time series

The $[CH_4]$ / $[C_2H_6]$ ratios for both pipelines varied between 45 and 15, representing approximately 2–6% C_2H_6 in pipeline gas by volume (Higher-chain hydrocarbons such as propane and butane typically account for ∼1% by volume of the natural gas in the Algonquin and Tennessee pipelines). The $[CH_4]$ / $[C_2H_6]$ ratio of pipeline gas sometimes varied at relatively short time scales, especially in the Algonquin pipeline

(Fig. 2.4, bottom panel). In contrast, $[CH_4]$ / $[C_2H_6]$ of the Tennessee pipeline remained relatively constant at ∼40, or 2.5% C_2H_6. The high variability in the $[CH_4]$ / $[C_2H_6]$ of the Algonquin pipeline is most obvious in 5 large excursions to low $[CH_4]$ / $[C_2H_6]$ during the winters of 2012-3 and 2013-4. These spikes are likely due to the input of LNG into the pipeline system during the winter. There are numerous LNG storage facilities in the New England region of the US that are filled during the summer months when natural gas prices are lower and used to supplement supply during winter months when natural gas prices are higher (Tom Rogers, personal communication). There is also an LNG tanker ship terminal in Everett, MA, within ∼5 km of downtown Boston that receives deliveries of LNG during winter months which are likely injected into the urban pipeline network. However, the process of liquifying natural gas typically strips it of higher-chain hydrocarbons such as C_2H_6 (Woodcock and Gottlieb, 2000). Thus, LNG input would not lower the $[CH_4]$ / $[C_2H_6]$ ratio unless higher-chain hydrocarbons were added along with LNG to maintain the heating value of the resulting natural gas mixture.

We created a combined $[CH_4]$ / $[C_2H_6]$ time series from the data for the Algonquin and Tennessee pipelines by weighting the individual data sets by the relative distribution station gas flow quantities (Fig. 2.4, bottom panel, in gray). This combined time series has no clear season pattern, with the exception of a few spikes to high $[C_2H_6]$ concentration during winter months, reflective of the source data in the Algonquin.

The constructed pipeline $[CH_4]$ / $[C_2H_6]$ time series agrees well with the $[CH_4]$/ $[C_2H_6]$ measured in both street and pipeline flask samples (Fig. 2.5, right panel). The $[CH_4]$ / $[C_2H_6]$ of our pipeline and street samples showed little seasonal variation, which is similar to the lack of seasonality in the pipeline $[CH_4]$ / $[C_2H_6]$ time series. Mean daily $[CH_4]$ / $[C_2H_6]$ values for pipeline and street flask samples were similar to pipeline time series $[CH_4]$ / $[C_2H_6]$ on corresponding days. The difference between

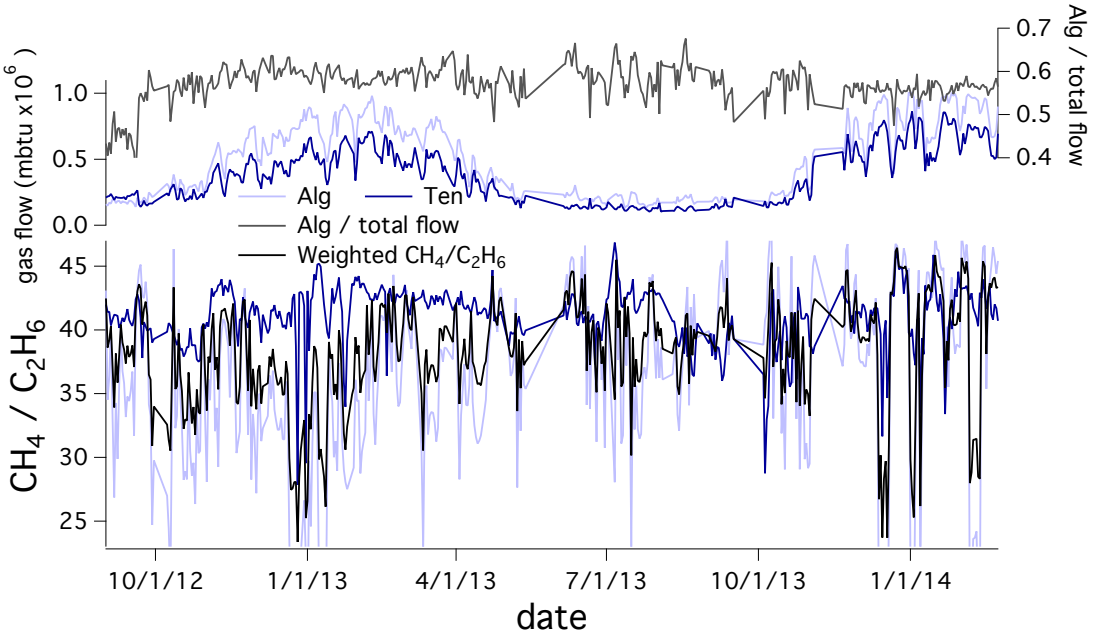

FIGURE 2.4: Time series of pipeline natural gas quality and quantity data. The amount of natural gas being transferred from the interstate pipeline system to the local distribution system is shown in the top panel (Algonquin pipeline in light blue and Tennessee pipeline in dark blue). The percentage of gas entering the local distribution system from the Algonquin pipeline is overlaid in gray, and varies between 50–65%, with a brief excursion to ∼40% in October of 2012. $[CH_4]$ / $[C_2H_6]$ ratio of pipeline gas is shown in the top panel. The combined $[CH_4]$ / $[C_2H_6]$ ratio, weighted by the relative gas capacity time series, is shown in black.

the daily mean of flask samples and constructed time series varied from as little as 0.4 on 8/20/2012 to as much as 33.5 on 8/21/2012. Likewise, street flask samples showed a range of agreement with the constructed $[CH_4]$ / $[C_2H_6]$ time series. The difference between flask and pipeline $[CH_4]$ / $[C_2H_6]$ varied from less than 5 (two days) to as much as 33.3 (one day). Despite the large differences between $[CH_4]$ / $[C_2H_6]$ of flask samples and our constructed $[CH_4]$ / $[C_2H_6]$ pipeline time series on some days, pipeline and street flask samples were much more similar to the constructed $[CH_4]$ / $[C_2H_6]$ time series than any of our biogenic samples, providing further evidence that our street samples are representative of pipeline gas.

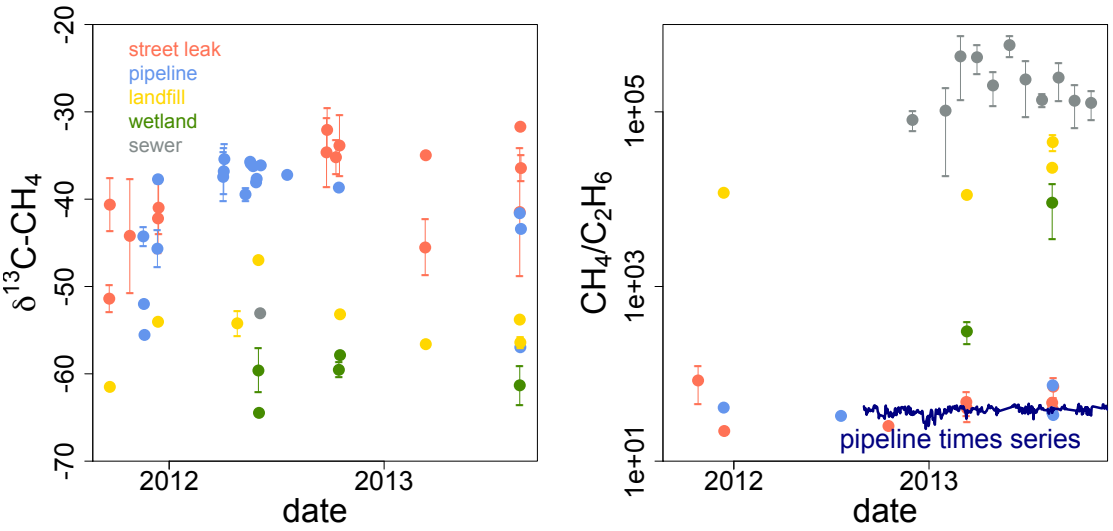

FIGURE 2.5: Time series of δ^{13}C-CH_4 (left) and $[CH_4]$ / $[C_2H_6]$ (right) point source measurements, with pipeline $[CH_4]$ / $[C_2H_6]$ time series superimposed. Circles represent mean for each type of sample on each day that samples were collected, and bars represent 1.5 daily interquartile range. Both pipeline and street point source $[CH_4]/[C_2H_6]$ ratios are consistent with pipeline methane/ethane ratio derived from the public records (i.e. Fig. 2.4).

2.4.3 Mobile surveys of potential methane sources

Of the five categories of non-biological potential point sources of CH_4 that we tested using mobile $[CH_4]$ surveys (gasoline filling stations, CNG filling stations, CNG bus depots, an LNG import terminal, and an LPG storage tank), gasoline filling stations and LPG storage do not appear to be a substantial source of urban anthropogenic CH_4. The $[CH_4]$ that we measured at 12 of the 13 gasoline filling stations and the one LPG storage tank was statistically indistinguishable from or significantly less than background $[CH_4]$, indicating that $[CH_4]$ measured on streets is higher than that measured while parked at these facilities. This is consistent with work by Peischl et al. (2013), who found that evaporated gasoline and LPG could be a source of higher-chain hydrocarbons, but not CH_4. The one gasoline filling station that was significantly higher than background was located on a Commonwealth Avenue,

a street that is known to have large leaks in the underground natural gas infrastructure and was documented as such in Phillips et al. (2013). It is likely that the elevated [CH_4] observed at that gasoline station was a result of [CH_4] wafting from nearby natural gas infrastructure leaks, which were higher in [CH_4] than background measured on streets more than 0.5 km distant. The [CH_4] measured while parked at the gasoline station was less than that measured on the surrounding streets. Based on our measurements, we see no evidence for large CH_4 plumes or smaller point-source emissions from evaporating hydrocarbons at gasoline filling stations or LPG storage tanks.

In contrast, the CNG filling stations that we measured were leaking CH_4 to the atmosphere. During every survey of both CNG stations, [CH_4] was significantly elevated relative to background [CH_4] within a $\sim$5 m radius of the CNG infrastructure (including pumps, compressors, etc.). During one [CH_4] measurement survey, we observed >20 ppm methane 2 m downwind of a CNG fueling pump compressor (Fig. 2.6, top panel). During this same survey, we observed plumes of CH_4 downwind of the CNG fueling pump compressor.

We found evidence for smaller but non-negligible CH_4 emissions from CNG bus fueling depots. There are two bus depots that house and fuel all of the 360 CNG buses run by the Massachusetts Bay Transit Authority (Boston Transit eMuseum, 2013), the only mass transit bus provider in the Boston metro area. These two bus depots are located in the neighborhoods of Jamaica Plain and Dorchester (JP and DOR hereafter). The DOR LNG bus depot showed evidence of some temporally variable CH_4 emissions. On two of our three surveys at the DOR LNG bus depot, [CH_4] measured $\sim$30 m downwind of LNG fueling infrastructure were significantly below background levels. We believe this to be because we were parked on the bus depot property, which is not underlain by natural gas infrastructure and thus not as susceptible to natural gas leaks as street measurements. On one evening survey

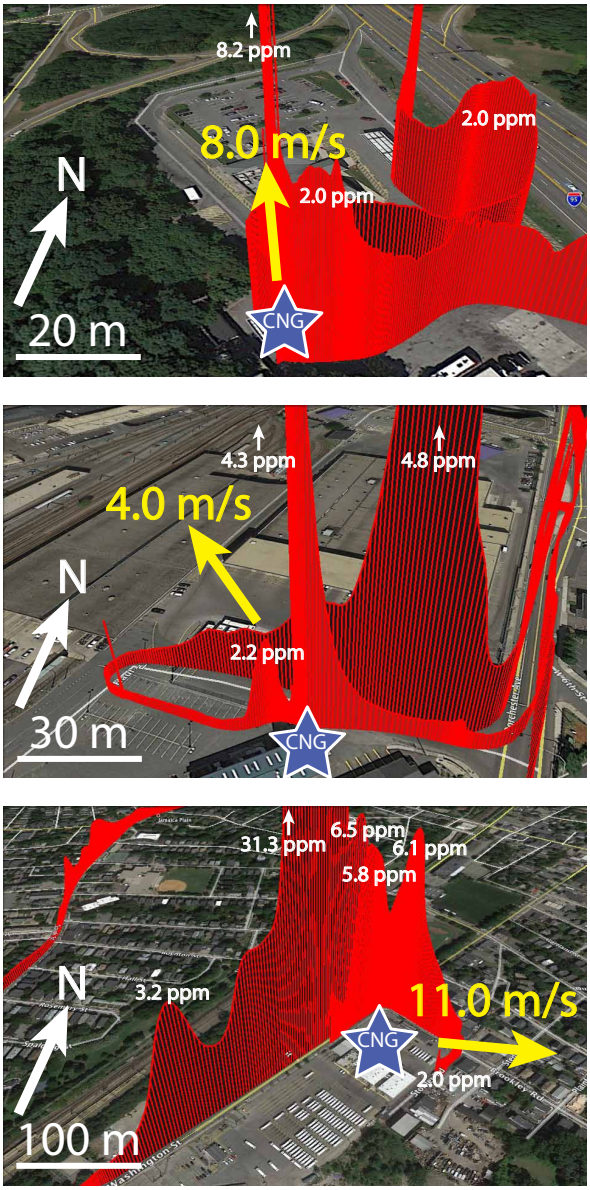

FIGURE 2.6: Mobile surveys of compressed natural gas (CNG) facilities (red stars). [CH_4] measurements are shown in red. Wind speed and direction are shown in each panel in yellow. Horizontal scale bars are shown in white, and are different for each panel. The vertical scale for CH_4 measurements of the top two panels is magnified five times relative to the bottom panel. Top: survey of a CNG filling station in December, 2012, showing high [CH_4] near the facility, with some CH_4 peaks downwind of the facility. CNG filling stations had elevated [CH_4] within ~5 m of facilities during all surveys that we conducted. Middle: Dorchester CNG bus depot in December, 2012, with peaks indicating CH_4 emissions, possibly due to bus fueling. Bottom: Jamaica Plain CNG bus depot in August, 2013, with very large CH_4 emissions on the westerly adjacent street, likely due to infrastructure leaks, and much smaller [CH_4] downwind of the CNG bus depot.

when buses were fueling, we observed [CH_4] above background levels, with transient peaks up to 4.8 ppm CH_4 within about 10 m of the fueling station (Fig. 2.6, middle panel). We observed these peaks while busses were fueling, and thus it seems likely that some CH_4 is emitted to the atmosphere during the bus fueling process.

Measurement of emissions from the JP LNG bus depot is complicated by the large number of CH_4 leaks on the road immediately adjacent to the depot. We repeatedly measured [CH_4] > 10 ppm on this street, and this potentially large source of CH_4 is difficult to distinguish from CH_4 emitted from the bus depot itself. We expect these areas of high [CH_4] on the street adjacent to the JP bus depot are due to underground infrastructure leaks, as the location of the elevated [CH_4] from the street did not change between dates and we found elevated [CH_4] in street manholes. Because these infrastructure leaks are located on the upwind side of the JP LNG bus depot, this facility had significantly lower [CH_4] downwind of the depot, farther from the street leak source, than upwind on all three sampling dates (Fig. 2.6).

Measurements downwind of the LNG import terminal were not significantly elevated relative to background during any of our surveys. This facility is large (~0.7 km^2), comprising many tanks and other infrastructure, and road access near the facility is restricted. We took our measurements ~100 m from the facility. Although there could be smaller CH_4 emissions from portions of this facility that we were unable to measure at such distances, we saw no evidence for large CH_4 plumes during our surveys.

Although we did not measure CH_4 emissions from vehicle traffic directly in this study, our driving surveys show no detectable enhancement of CH_4 when other cars are present. Multiple previous studies have also found vehicle traffic to be an insignificant source of urban CH_4 (Townsend-Small et al., 2012; Mays et al., 2009), as three-way catalyst technology significantly reduced hydrocarbon emissions from passenger cars (Heeb et al., 2003). Thus, it is unlikely that vehicle traffic in urban

Boston impacted our mobile [CH_4] surveys.

2.5 Conclusions

Partitioning CH_4 among various sources is important to understand the regional CH_4 budget and to reduce CH_4 emissions, particularly in urban areas. By measuring $\delta^{13}C$ and [CH_4] / [C_2H_6] of urban [CH_4] sources in Boston, MA, USA, we have shown that CH_4 measured on streets is most likely due to leaks in natural gas infrastructure. We have also created a time series of [CH_4] / [C_2H_6] for pipeline natural gas entering the Boston area, which agrees well with our flask samples of pipeline gas and provides further support that the methane that we observed on the streets in Boston is due to natural gas infrastructure leaks. We found the [CH_4] / [C_2H_6] ratio to be a powerful tool to differentiate CH_4 sources, and our time series of pipeline [CH_4] / [C_2H_6] could be used to partition CH_4 sources in top-down estimates of CH_4 at the city or regional level in the future.

We also investigated CH_4 emissions from other potential urban CH_4 sources using a mobile CRDS instrument. We found that the gasoline filling stations and LPG storage facilities that we measured are not obvious sources of CH_4. CNG filling stations, on the other hand, could be sources of CH_4, either continuously in the case of the commercial filling stations that we measured, or intermittently during vehicle fueling, as we observed at a CNG bus depot.

Our results provide more robust support for the conclusions of Phillips et al. that natural gas infrastructure is the dominant source of CH_4 emissions on roadways in Boston and likely other urban areas. Moreover, we found that the [CH_4] / [C_2H_6] ratio of CH_4 point sources provides greater partitioning than $\delta^{13}C$ between biogenic and thermogenic sources. The addition of the time series of [CH_4] and [C_2H_6] in the pipeline in conjunction with point source measurements could be used to evaluate CH_4 flux at a regional level in the future. In our survey measurements of potential

anthropogenic CH_4 sources other than pipelines, we did not find any CH_4 plumes that would likely be comparable with pipeline emissions. Thus, it appears that pipeline leaks are the dominant source of non-biogenic methane in the Boston urban area.

The bottom-up CH_4 source apportionment presented in this paper will be used in future work (in preparation) to develop a top-down estimate of the overall CH_4 flux from the Boston area and partition the flux between CH_4 sources. Moreover, these isotopic and higher-chain hydrocarbon signatures are likely representative of urban CH_4 sources in other cities.

Improved CH_4 identification techniques can better partition the urban CH_4 budget and can assist efforts to identify and fix urban gas leaks. Reducing CH_4 leaks from infrastructure, like those measured in this study, prevents further greenhouse gas emissions, saves money for natural gas consumers and distribution companies, and improves the safety of urban areas for utility workers and the general public.

Acknowledgement

This work was supported by the Environmental Defense Fund and the Duke Nicholas School of the Environment.

Appendix 2A: Experimental procedures for GC-FID calibration and analysis

Table 2.1: Standard gases used for hydrocarbon quantification with GC system. Each standard gas was injected into the GC system in 250 μl and 1000 μl aliquots.

$[CH_4]$ (ppm)	$[C_2H_6]$ (ppm)	supplier
50	10	Airgas
100	100	Air Liquide
1000	1000	Scott (of Air Liquide)
1000000	0	Air Liquide
0	1000000	Air Liquide

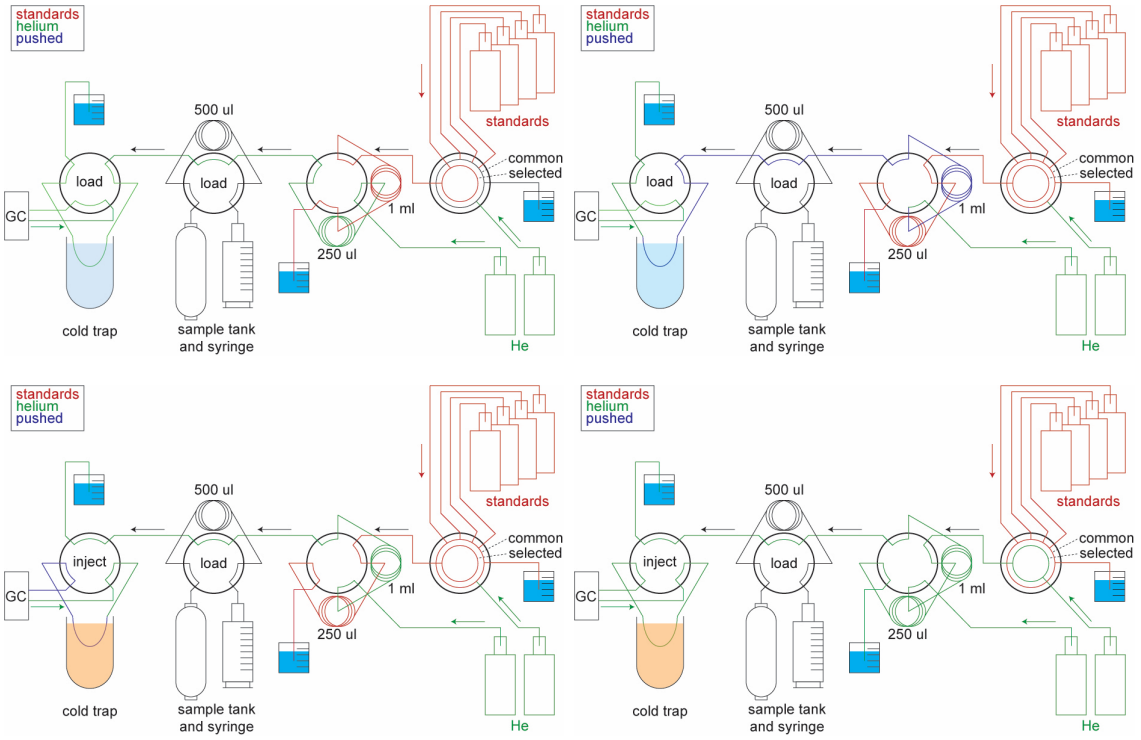

FIGURE 2.7: GC system for hydrocarbon quantification. Four panels illustrate standard injection process sequentially. Sample injection process is similar. Top left: Standard gas (red) is selected using a 12-port valve. Gas flows through a sample loop (either 250 ml or 1000 ml) and out to a submerged vent. Sample loop volume is selected using an 8-port valve. Top right: Sample loop volume is changed on 8-port valve. Helium carrier gas (green) flushes standard gas in the sample loop (blue) onto the cold trap, which is cooled by submersion in liquid N (light blue). Bottom left: 6-port valve connected to cold trap is switched from load position to inject position, putting the cold trap with frozen hydrocarbons in line with the GC inlet. The cold trap is then rapidly heated with a beaker of boiling water (orange) to release the hydrocarbons onto the GC. Bottom right: System is flushed with helium to prepare for the next standard. Samples are loaded similarly to standards, with a syringe used to draw sample gas from a sampling tank through a 500 ml loop

3

Partitioning the biological and thermogenic contribution to the total methane flux in Boston, MA

3.1 Abstract

Urban areas are potentially large but relatively poorly quantified sources of methane (CH_4), a potent greenhouse gas and precursor to ground-level ozone. Effective emissions reduction strategies will require a better understanding of the urban methane budget, including the relative strength of CH_4 sources in the urban environment. To partition the urban CH_4 flux in Boston, MA between biological (wetlands, landfills, and wastewater treatment) and thermogenic (natural gas transportation and infrastructure) CH_4 sources, we measured CH_4 and ethane (C_2H_6) concentrations, as well as the carbon isotopes of CH_4, on a rooftop in Boston. Comparing rooftop measurements to a time series of pipeline natural gas [CH_4] and [C_2H_6], we found that 88% of the CH_4 enhancement that we observed in the air over Boston was attributable to thermogenic sources, likely natural gas infrastructure (95% bootstrap confidence interval: 82–94%). A first-order estimate of CH_4 flux suggests that the natural gas

infrastructure in Boston could be leaking 14 g CH_4 per m^2 per year (95% CI: 12–16 g CH_4 per m^2 per year), or 180 Gg CH_4 per year (95% CI: 150–210 Gg CH_4 per year). Carbon isotopes of CH_4 further confirmed the source of a subset of peaks that had relatively large CH_4 enhancements (>1000 ppb) as either biological or thermogenic. The large amount of thermogenic CH_4 that we found in the atmosphere in Boston is consistent with past studies that have documented leaks in the city's urban natural gas distribution system and suggests that fixing these leaks could have a large and immediate impact in reducing Boston's greenhouse gas emissions.

3.2 Introduction

Methane (CH_4) is a powerful greenhouse gas with a warming potential 84 times greater than that of carbon dioxide over a 20-year time horizon (Stocker et al., 2013). Atmospheric CH_4 concentration has increased more than 2.5-fold from pre-industrial levels, from ~680 ppb to ~1800 ppb currently, and is responsibly for roughly one third of current anthropogenic radiative forcing (Butler, 2011). Anthropogenic emissions account for ~60% of the global total CH_4 budget of 580 Tg per year. Of that, the US accounts for roughly 58.5% of global anthropogenic CH_4 emissions (U.S. Environmental Protection Agency, 2011).

Recent research has suggested that urban areas may be large sources of CH_4 to the atmosphere (Table 3.1), possibly representing 21–34% of global anthropogenic CH_4 emissions (Wunch et al., 2009). However, considerable uncertainty remains in the CH_4 budget, both globally and specifically for urban areas (Kirschke et al., 2013). Natural gas infrastructure is the largest anthropogenic CH_4 source in the US (U.S. Environmental Protection Agency, 2011), and the few studies that have quantified the contribution of natural gas infrastructure to urban CH_4 emissions have found it to be large (Table 3.1), ranging from 20% to >50% of total CH_4 emissions in some cities.

Table 3.1: Urban CH_4 emissions estimates

Location	CH_4 flux (Gg/year)	CH_4 from NG infrastructure	Source
Amsterdam, Netherlands	1.77	25%[a]	Veenhuysen and Hofschreuder (1995)
London, England	240 - 312	20%	Lowry et al. (2001)
Moscow, Russia	60		Zinchenko et al. (2002)
Krakow, Poland		>50%	Kuc et al. (2003)
St. Petersburg, Russia	100		Nisbet (2005)
Los Angeles, USA	600 ± 100		Wunch et al. (2009)
Los Angeles, USA		>50%	Townsend-Small et al. (2012)

[a] Authors also found that 47% of national CH_4 emissions from NG distribution

CH_4 sources differ in the amount of C_2H_6 that they produce, an observation that has been used in previous research to partition CH_4 sources in urban areas (e.g. Wennberg et al. (2012), also see previous chapter) and track changes in the CH_4 budget globally (Aydin et al., 2011; Simpson et al., 2012). Biological CH_4 sources, such as wetlands, landfills, and wastewater treatment, typically do not produce hydrocarbons other than CH_4 (Rudolph, 1995). CH_4 from geological deposits formed under heat and pressure, so-called thermogenic CH_4, can co-occur with C_2H_6 and other hydrocarbons. These hydrocarbons are extracted together and the resulting natural gas sold to consumers can contain up to ∼5% C_2H_6 by volume.

To better understand the relative strength of biological and thermogenic CH_4 sources in urban areas, we measured CH_4 and ethane (C_2H_6) concentration, as well as carbon isotopic composition of CH_4 (δ^{13}C-CH_4) of the atmosphere over Boston, MA, USA for three months in the winter of 2012–2013. This flux partitioning between broad classes of CH_4 sources, when combined with forthcoming results of an inverse modeling estimate of total CH_4 flux from Boston, will help construct a more detailed CH_4 budget for the urban area. In lieu of an inverse modeling estimate, we obtain

a first-order estimate of the CH_4 emissions from Boston based on the amount of natural gas entering the city. A better understanding of urban CH_4 emissions can inform targeted CH_4 emissions reductions strategies. In addition to being a powerful greenhouse gas, CH_4 is a precursor to ground-level ozone, and thus reducing CH_4 emissions particularly in urban areas could have health benefits from avoided ozone pollution (Fiore et al., 2002).

3.3 Methods

3.3.1 Boston methane monitoring network

The instrument used to measure $[CH_4]$ and $[C_2H_6]$ in this study is part of a network of $[CH_4]$ measurement instruments around the Boston metro area (Fig. 3.1). The CH_4 monitoring network includes stations both upwind (Harvard Forest) and usually approximately downwind (Nahant) of the city, as weather patterns and wind in Boston most commonly move from west to east. There is also a $[CH_4]$ monitoring instrument installed near the top of the Prudential Tower, the second tallest building in downtown Boston (228 m), with atmospheric sampling inlets on the four corners of the building.

Data from this network of instruments will be used as part of an inversion model, similar to that utilized by McKain et al. (2012), to estimate the total CH_4 flux from the Boston area. The measurements and methodology described here will partition the overall flux estimate generated from the inversion model between biological and thermogenic CH_4 sources, thereby beginning to establish a detailed CH_4 budget for the urban area.

3.3.2 Rooftop hydrocarbon and meteorological measurement

$[CH_4]$, $[C_2H_6]$, and δ^{13}C-CH_4 were measured by infrared absorption spectroscopy using a continuous-wave quantum cascade laser (QCL) sensor (Aerodyne Research,

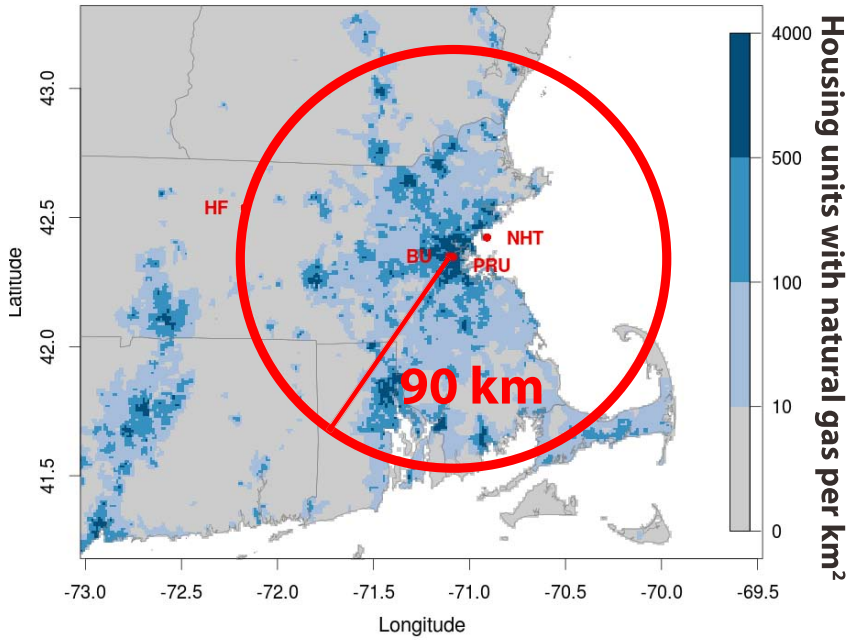

FIGURE 3.1: Location of [CH_4] and [C_2H_6] measurements collected at Boston University (BU, center, in red), along with the three additional [CH_4] monitoring instruments in the Boston-area CH_4 monitoring network (shown in red; PRU: Prudential Building, downtown Boston; NHT: Nahant; HF: Harvard Forest). The study area includes many residential natural gas customers (density shown in blue shading) in the Boston metro (center of study area), Providence, RI (south) and Nashua, NH (north). The 90 km boundary around BU (boundary and radius shown in red) defines the zone in which data from pipeline infrastructure was considering constructing our pipeline [CH_4] / [C_2H_6] signature.

Inc., Billerica, MA). The instrument is described in detail by Santoni et al. (2012). Briefly, the CW-TILDAS-76-CS instrument that we used operates by modulating current to the QCL to linearly scan the laser frequency across absorption lines for the gases of interest. The instrument that we employed used two QCLs in separate housings with analytical cavities connected in series, one to measure δ^{13}C-CH_4 and the other to measure [C_2H_6] and [CH_4]. The QCL cavities achieve a long effective path length (76 m) using multiple passes between mirrors spaced ~40 cm apart. A TriScroll 600 l/min pump (Varian TriScroll600) generated a flow rate of ~8 slpm through the sample cell (0.5 L volume at 4.0 kPa), corresponding to a cell time

constant of <1 s. At this flow rate, the CW-TILDAS-76-CS provides measurement precision of <0.05 ppb for [CH_4] and [C_2H_6], and an Allan variance of 2.85‰ over 1 s for δ^{13}C-CH_4 (Mark Zahniser, Aerodyne Research, Inc., personal communication).

The instrument was checked for drift in [CH_4] and [C_2H_6] four times per hour with two reference gases. Every 15 minutes, the instrument inlet was diverted from drawing atmospheric air to introduce either ultra high purity zero-CH_4 air (at minutes :00 and :30) or compressed air with [CH_4] and [C_2H_6] approximately at atmospheric ambient levels (at minutes :15 and :45; both reference gases from Airgas, Radnor, PA, USA). The instrument inlet was flushed with standard gas for 30 s before each 30-s calibration period. Similarly, δ^{13}C-CH_4 measurements were calibrated by injecting a reference gas once per hour with δ^{13}C-CH_4 measured independently at the Harvard Engineering School of Applied Sciences

We sampled from the rooftop of Boston University (685 Commonwealth Avenue, 42.350774 °N, 71.107489 °W). The sampling inlet was in the center of the rooftop of the building, ∼1.5 m from the surface of the roof and elevated ∼40 m above ground level. These rooftop measurements were collected for three months from November of 2012 through January of 2013. Meteorological conditions were measured by a CSAT3 three-dimensional sonic anemometer mounted on the same rooftop, described more fully in Briber et al. (2013).

3.3.3 Data processing and filtering

The purpose of this investigation was to compare the [CH_4] and [C_2H_6] that we observed on the rooftop to data from the pipeline natural gas in Boston. To allow this comparison and to ensure the quality of our rooftop data, we applied calibration shifts and filtered the data so as to analyze only time periods that best represented the well-mixed atmosphere above the city.

Rooftop [CH_4] and [C_2H_6] were corrected based on the measured values of the

zero and reference standard gases. A time-varying offset was applied to [CH_4] and [C_2H_6] (separately for each species) at each time point, if necessary, if either the [CH_4] or [C_2H_6] of the zero standard drifted >0.05 ppb from 0.00 ppb. Drift in the [CH_4] or [C_2H_6] of the reference gas was corrected with a time-varying multiplicative factor such that the difference between the zero and reference gas [CH_4] and [C_2H_6] remains constant throughout the dataset.

To remove the influence of very brief transient peaks in [CH_4] on the order of seconds, possibly due to local natural gas leaks or CH_4 sources on or near the building housing our instrument, we smoothed the data by taking the median of all measurement points (i.e. excluding calibration values, if any) in each non-overlapping five-minute period.

We applied two criteria to select only those periods in our data that best represented the well-mixed atmosphere. First, we considered only points during daytime hours, defined as 11:00 to 17:00 local time, during which the atmospheric boundary layer is high and circulation is greatest. We also excluded data from times in which the wind speed was < 2.0 m/s so as as to minimize the influence of CH_4 from sources near to or on the Boston University building.

To correct for the changing background of ambient [CH_4] and [C_2H_6] in the urban environment, we calculated [CH_4] and [C_2H_6] enhancements by comparing our measured [CH_4] and [C_2H_6] values to a time series approximating background calculated from the same [CH_4] and [C_2H_6] values. For each three-hour non-overlapping window in our data, we computed the 20^{th} percentile of both [CH_4] and [C_2H_6], which were then splined together using a third-order polynomial algorithm (Akima, 1970). The three-hour window was chosen to correspond to the approximate flushing time of the urban atmosphere, although the results are not strongly dependent on the choice of background window length (see results and discussion section below). At each time point, the difference between the measured value and this splined 20^{th}

percentile time series was considered to be the concentration enhancement, referred to hereafter as ΔCH_4 and ΔC_2H_6, respectively. It was these concentration enhancements that we compared to the $[C_2H_6]$ / $[CH_4]$ of pipeline natural gas in the Boston area.

To provide an independent test of our results, we employed an alternative analysis approach using the same filtered $[CH_4]$ and $[C_2H_6]$ data which did not rely on comparing measured concentrations to 20^{th} percentile values. Instead, we regressed $[CH_4]$ and $[C_2H_6]$ for each daytime period, taking the slope of the each least-squares regression as an estimate of $[C_2H_6]$ / $[CH_4]$ value for the given day. We kept only the estimates with $R^2>0.7$. We then compared the distribution of daily $[C_2H_6]$ / $[CH_4]$ estimates to the $[C_2H_6]$ / $[CH_4]$ ratio of pipeline natural gas.

3.3.4 Bootstrapping uncertainty analysis

We used a bootstrapping approach to evaluate the robustness and uncertainty in our CH_4 source appointment algorithm (Clark, 2007). In this approach, the analysis being evaluated (in our case, the determination of the percent of CH_4 enhancement that is due to thermogenic sources) is performed on a subset of the original data set using random sampling with replacement. This resampling and analysis is repeated many times (we used $N = 10^6$), and the resulting values of the parameter were estimated from a distribution that provides insight into the bias, robustness, and confidence intervals for the estimator. Any disagreement between the mean of the bootstrap distribution and the original estimate is evidence of possible bias, and asymmetry of the the bootstrap distribution can indicate that the original estimate is not robust against outliers (Clark, 2007). If the bootstrap distribution is normal and its mean is equal to the original parameter estimate, then the statistics of the bootstrap distribution, such as the standard deviation, can be used to construct a lower bound on the experimental uncertainty (e.g., Allen et al., 2013).

3.3.5 Pipeline natural gas data

We compared the $[CH_4]$ and $[C_2H_6]$ measured on the rooftop of BU to the $[CH_4]$ and $[C_2H_6]$ of pipeline natural gas reconstructed from public records. The construction of this time series is described more fully in the previous chapter. We considered all interconnections between the low-pressure natural gas distribution system and the three interstate pipelines in the Boston area (Algonquin; Tennessee; and Maritimes and Northeast) that are within 90 km of Boston. The C_2H_6 and higher-chain hydrocarbon concentration of the natural gas is also recorded at a subset of these information stations. The amount and composition of gas that passes through these stations is recorded and posted online by the Federal Energy Regulatory Commission to ensure that natural gas transport companies deliver gas with sufficient heating value. To construct a time series of pipeline $[C_2H_6]$ / $[CH_4]$, we took an average of the $[C_2H_6]$ / $[CH_4]$ of each individual pipeline weighted by the amount of gas flowing from that pipeline into the low-pressure distribution system within the study area.

Because of the temporal variability in the pipeline data set and the unknown lag time between the pipeline data and the CH_4 observed at the rooftop level, we applied a seven-day moving average to the pipeline $[C_2H_6]$ / $[CH_4]$ time series. We then used the median $[C_2H_6]$ / $[CH_4]$ of this smoothed time series from the time period corresponding to our atmospheric data as the pipeline $[C_2H_6]$ / $[CH_4]$ signature to which we compared the C_2H_6 and CH_4 enhancement measured on the rooftop.

3.3.6 Total CH_4 flux estimate

To obtain a first-order estimate of the amount of CH_4 emitted by the Boston urban area, we used an emissions factor for CH_4 leakage as a percentage of pipeline natural gas delivered to Boston. McKain et al. (2014, in preparation) found that 2.8–3.8 of the natural gas delivered to the Boston area enters the atmosphere as uncombusted CH_4, which we combined with our pipeline natural gas delivery data to estimate the

total CH_4 emissions for Boston. We converted the amount of natural gas entering Boston, as reported by pipeline companies in MMbtu per day, to grams delivered per day using the standard industry conversion of 1 MMbtu = 1.054615 GJ (Alberta Department of Energy, 2014) and combustion enthalpies of 891.0 and 1560.7 GJ per mol for CH_4 and C_2H_6, respectively (Kaye and Laby, 2013). CH_4 emissions per unit area were calculated by computing the approximate land area contained in the 90-km-radius study area (Fig. 3.1), $1.272 \cdot 10^4$ km^2.

Because natural gas consumption in Boston is strongly seasonal (Fig. 3.4), we integrated daily CH_4 emissions from uncombusted natural gas for all of 2013 to construct an annual emissions estimate. Cumulative CH_4 emissions rates for all sources, including both biogenic and thermogenic, were constructed by dividing annual natural gas emissions rates by 0.88, our estimate of the fraction of CH_4 emissions in Boston attributable to thermogenic sources.

Uncertainty in the resulting annual emissions rates were created by combining uncertainties from individual parameters in quadrature (Taylor, 1996). In particular, combining the uncertainty in the amount of natural gas that is is emitted as uncombusted CH_4 (95% CI: ±5%) with that in the amount of atmospheric CH_4 in Boston that is due to thermogenic sources (95% CI: ±6%),

$$\sigma_{\text{total}} = \sqrt{\left(\frac{0.005 \cdot 0.51}{0.033}\right)^2 + \left(\frac{0.06 \cdot 0.51}{0.88}\right)^2} \tag{3.1}$$

$$= 0.085, \tag{3.2}$$

suggesting a 95% confidence interval ($\pm 1.96\sigma$) of ± 17%.

3.4 Results and discussion

We observed $[CH_4]$ between ∼2000–3000 ppb in our rooftop measurements, with typical values below 2200 ppb (Fig. 3.2). $[C_2H_6]$ ranged from ∼2 ppb to as high

as 25 ppb. We observed a diurnal pattern of CH_4 buildup during the night and lower [CH_4] during the day, consistent with CH_4 buildup under a stable nocturnal boundary layer, although the magnitude of this enhancement (∼200 ppb) was smaller than that measured in some other urban areas (e.g. Lowry et al., 2001).

Enhancements in [CH_4] and [C_2H_6] often co-occurred in our data, with C_2H_6 enhanced relatively more than CH_4, leading to an elevated C_2H_6 to CH_4 ratio (Fig. 3.2, bottom panel). This elevated C_2H_6 to CH_4 ratio is indicative of a pipeline CH_4 source. The Major Axis (MA; Samuelson, 1942) linear fit to the daytime ΔCH_4 and ΔC_2H_6 data has a slope of 0.0247, which is similar to that of the pipeline mixing line (0.0281) from the median [C_2H_6] / [CH_4] of our smoothed pipeline time series (Fig. 3.3). Taking the ratio of the slope of the linear fit of the daytime ΔCH_4 and ΔC_2H_6 to the slope of the pipeline mixing line yields 0.88, suggesting that 88% of the CH_4 enhancement that we observed was due to pipeline natural gas, following Wennberg et al. (2012). Infrastructure leaks are a known source of atmospheric emissions in Boston (Phillips et al., 2013), and are the most likely source of the thermogenic gas that we observed (see chapter 2).

Our estimate of the total CH_4 emissions from Boston are comparable to other large cities, but the fraction of CH_4 attributable to pipeline natural gas is likely higher. The total CH_4 flux from Boston based on a 3.3% leakage rate of natural gas delivered to Boston during 2013 (Fig. 3.4) is 180 Gg (95% CI: 150–210 Gg CH_4 per year), or 14 g CH_4 per m^2 per year (95% CI: 12–16 g CH_4 per m^2 per year). This flux estimate is comparable to CH_4 emissions estimates for other large cities, such as Moscow(Zinchenko et al., 2002) and London(Lowry et al., 2001). However, our estimate of the percentage of CH_4 attributable to natural gas infrastructure in Boston (88%) is greater than that estimated in London (∼20%).

Bootstrapping our CH_4 partitioning algorithm provides relatively tight bounds on our CH_4 partitioning estimate. The distribution resulting from bootstrapping

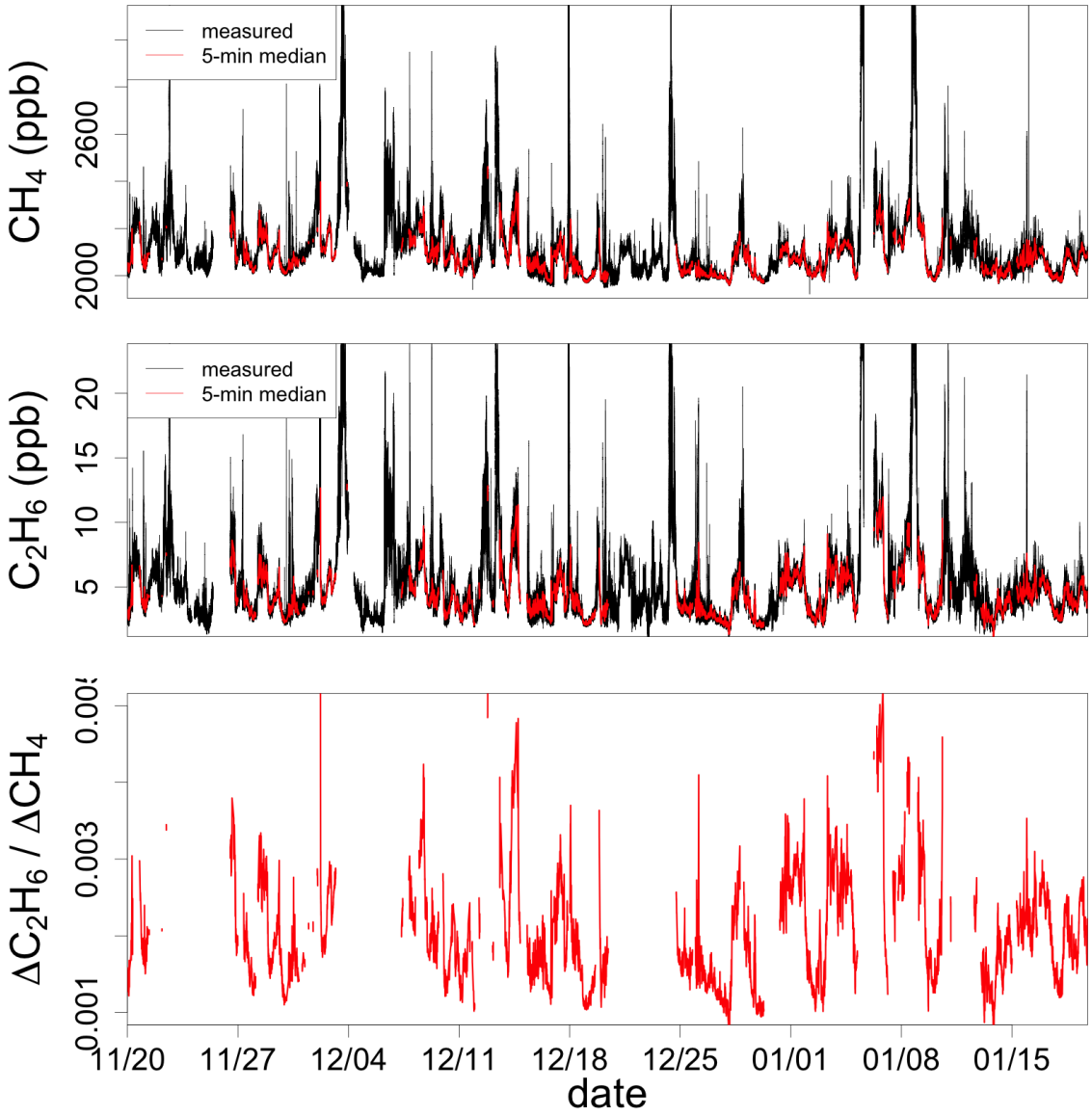

FIGURE 3.2: Time series of $[CH_4]$ (top panel) and $[C_2H_6]$ (middle panel) measured on the Boston University rooftop. Time series show both measured (black) and smoothed fit to data (red, splined 3-hour block 20^{th} percentiles, described in text). The difference between the respective smoothed and measured values for $[CH_4]$ and $[C_2H_6]$ is used to calculate the ratio of $[C_2H_6]$ enhancement (ΔC_2H_6) to $[CH_4]$ enhancement (ΔCH_4, bottom panel). Co-occurrence of CH_4 and C_2H_6 excursions lead to elevated ΔC_2H_6 / ΔCH_4 ratio and are indicative of thermogenic CH_4 emissions.

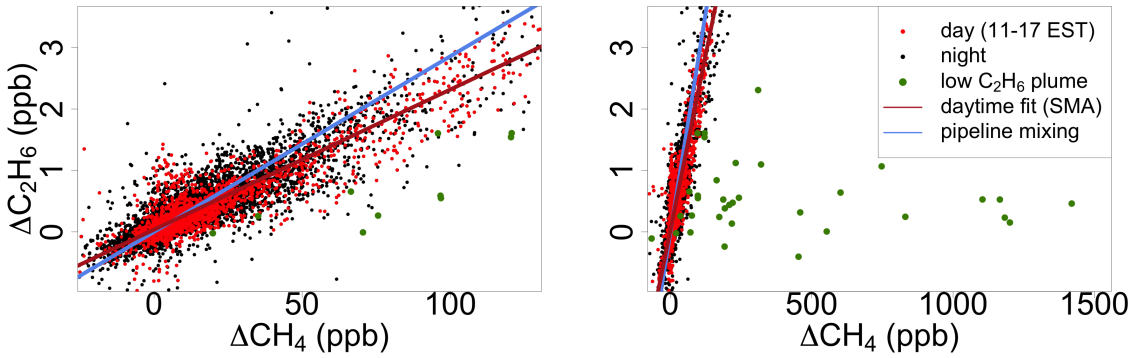

FIGURE 3.3: CH_4 and C_2H_6 enhancement above smoothed time series of 20th percentile values. CH_4 and C_2H_6 enhancements co-occur in both day (red dots) and night (black dots) periods. The slope of the major axis (MA) fit to the daytime data (dark red; slope = 0.0247) agrees well with the slope of the pipeline natural gas mixing line (light blue; slope = 0.0281) constructed from pipeline company data. The ratio of slopes of the MA fit to the pipeline mixing line suggests that 88% of the CH_4 enhancement that we observed is due to pipeline sources. Despite the predominantly thermogenic emissions, we did observe several periods of elevated CH_4 without a corresponding increase in C_2H_6 (green dots, left panel shows greater ΔCH_4 range) indicative of a transient biological CH_4 source, likely a nearby wastewater treatment facility (see Fig. 3.8)

our analysis 100,000 times is highly normal (Fig. 3.5), with a mean of 88.1 and a standard deviation of 3.2. The agreement between our CH_4 partitioning algorithm and the bootstrapping distribution mean demonstrates that our algorithm is robust against outliers in ΔCH_4 and ΔC_2H_6. The 95% confidence interval resulting from this bootstrapping for our estimate of the percentage of the observed CH_4 enhancement due to pipeline natural gas is 82–94%.

Automobile and compressed natural gas bus traffic do not appear to be major contributors to the CH_4 enhancement that we observed. Considering only data from weekdays (Monday through Friday), and excluding weekend days when vehicle traffic is lower, our partitioning algorithm produced an estimate of 89.0% for the amount of observed CH_4 enhancement due to pipeline sources, which is within the 95% confidence interval of our original estimate. Similarly, excluding holiday periods when many business are closed and vehicular traffic is lower did not significantly

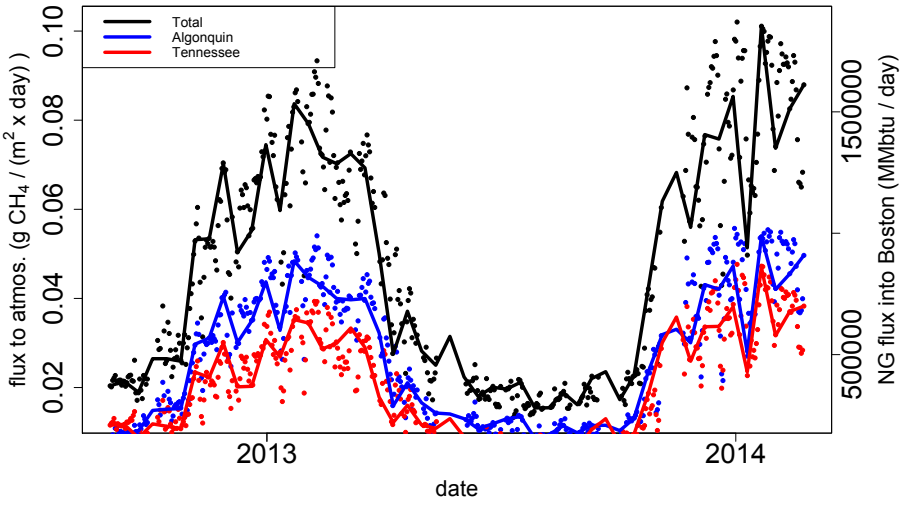

FIGURE 3.4: Daily flux estimate for Boston study area, assuming 3.3% of the natural gas that enters the study area is lost as uncombusted CH_4. Points represent daily pipeline capacity for and Algonquin (blue) Tennessee (red) pipelines, with total in black. Smoothed splines are created with a 10-day moving average window. CH_4 emissions are estimated to be higher in the winter, when natural gas use is greatest. Integrating the total daily CH_4 emissions over 2013 yields a total flux of 14 g CH_4 per m^2 per year (95% CI: 9–19 g CH_4 per m^2 per year), or 180 Gg CH_4 per year from our study area (95% CI: 120–240 Gg CH_4 per year).

influence our CH_4 enhancement apportionment. When we excluded data from the American Thanksgiving holiday (Nov. 21 to 23, 2012) and Christmas/New Years holiday (Dec. 24, 2012 to Jan. 1, 2013), we found that our apportionment of CH_4 enhancement, 87.5% due to pipeline natural gas, was still within the 95% confidence interval of our original estimate. Other studies of urban CH_4 emissions have also found that vehicles are not significant CH_4 sources since the introduction of modern catalytic converter technology (Mays et al., 2009; Townsend-Small et al., 2012).

Changing the way in which the pipeline [CH_4] and [C_2H_6] signature was computed also did not have a significant impact on our resulting partitioning of biological and thermogenic CH_4. In our original analysis, we used the median pipeline [C_2H_6] / [CH_4] value for the entire time period of our atmospheric measurements. Aggregating over this long time period could neglect shorter-term variations in pipeline [CH_4]

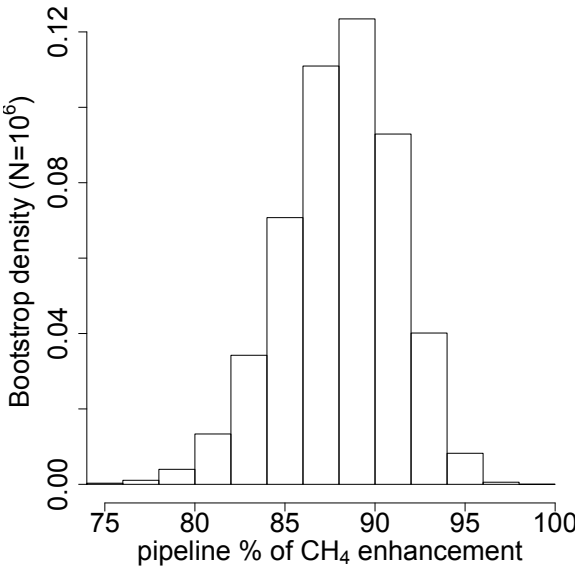

FIGURE 3.5: The mean estimate of pipeline CH_4 contribution to urban atmospheric CH_4 enhancement above background [CH_4] from bootstrapping our CH_4 enhancement partitioning algorithm is 88.1%, in agreement with our original estimate. Based on the standard deviation of the bootstrapping distribution (3.2) , the 95% confidence interval for our estimate of pipeline CH_4 contribution to total CH_4 enhancement is 82.0–94.4%.

and [C_2H_6]. Thus, we tried using both monthly and weekly pipeline [C_2H_6] / [CH_4] medians, although neither change significantly impacted our results. For monthly tests, we compared all of the atmospheric data collected in each month with the rooftop ΔCH_4 and ΔC_2H_6 for the same month. Doing so, we found the mean of the three monthly estimates (for Nov and Dec, 2012 and Jan, 2013) of pipeline natural gas enhancement to atmospheric [CH_4] was 83%, similar to, and within the 95% confidence interval of, our original estimate of 88%. For weekly analyses, we similarly computed the median pipeline [C_2H_6] / [CH_4] value for each week and compared it to that of the rooftop measurements for that week. We found that the distribution of weekly estimates had a mean of 83%, also within the 95% confidence interval of our original estimate.

Our results were further confirmed by an alternative analysis approach in which

we estimated daily atmospheric $[C_2H_6]$ / $[CH_4]$ values using linear regression. We used the slope of the linear regression of $[C_2H_6]$ to $[CH_4]$ from the daytime period of each day as an estimate of the $[C_2H_6]$ / $[CH_4]$ of the atmospheric CH_4 enhancement (Fig. 3.6). The distribution of daily $[C_2H_6]$ / $[CH_4]$ estimates from days that had R^2>0.7 had a mean of 0.025 (95% confidence interval: 0.023 - 0.027). Comparing to the $[C_2H_6]$ / $[CH_4]$ ratio of pipeline gas (0.0281) suggests 89.0% of the CH_4 enhancement that we observe is due to pipeline natural gas (bootstrapped 95% confidence interval: 80.7–98.2), which is in good agreement with our previous estimate of 88%.

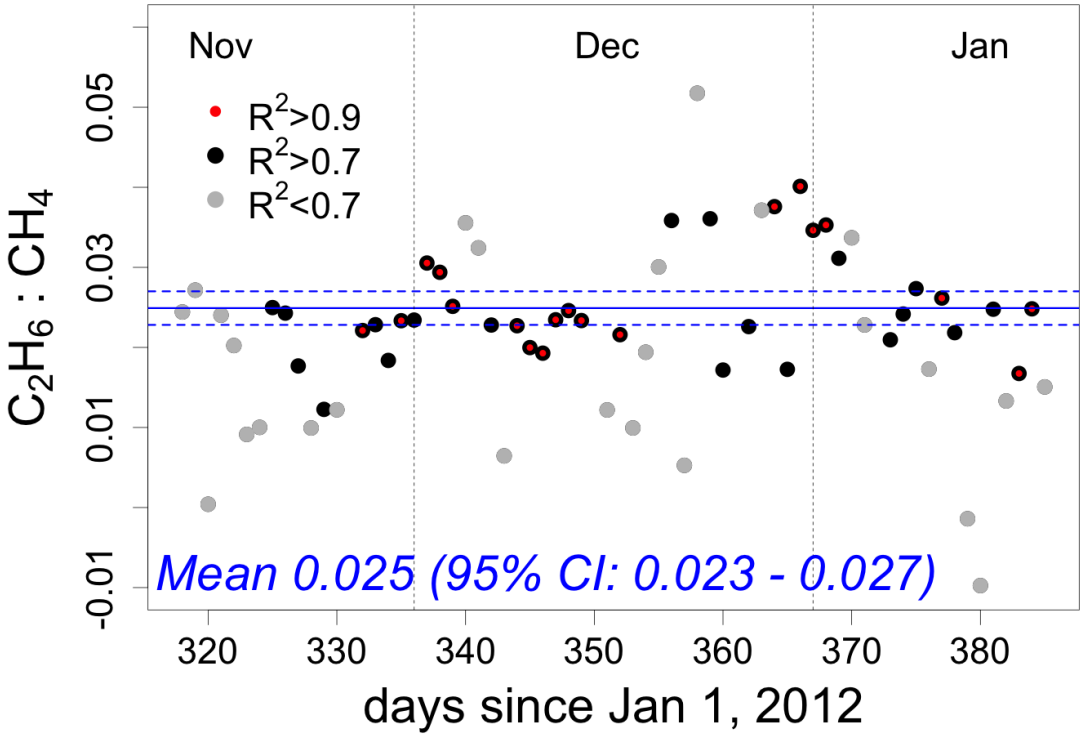

FIGURE 3.6: Daily slope of the regression $[C_2H_6]$ to $[CH_4]$ for daytime hours. Days high R^2>0.7 are indicated in black, and those with R^2>0.9 are shown in black with red centers. The mean $[C_2H_6]$ / $[C_2H_6]$ for all days with R^2>0.7 was 0.0249 (solid blue line, 95% confidence interval denoted with dashed blue lines). The mean daily $[C_2H_6]$ / $[C_2H_6]$ agrees with the $[C_2H_6]$ / $[C_2H_6]$ of pipeline natural gas in Boston during our study period ().

We found that δ^{13}C-CH_4 was useful for confirming CH_4 enhancements as being either biogenic or thermogenic as suggested by the ΔC_2H_6 / ΔCH_4 ratio. We used Keeling plots (Pataki et al., 2003) to identify the δ^{13}C-CH_4 of the source of CH_4 enhancements (Fig. 3.7), in which the vertical intercept of the least-squares fit to δ^{13}C-CH_4 as a function of $1/CH_4$ is taken to be the δ^{13}C-CH_4 value of the source of the CH_4 enhancement. Because of the large variability in our δ^{13}C-CH_4 data, the Keeling plot analysis was most successful in identifying the δ^{13}C-CH_4 signature of peaks with a large range in $[CH_4]$. In the two-week time period for which δ^{13}C-CH_4 data were available, there were two periods in which $[CH_4]$ exceeded 2400 ppb (Fig. 3.7, top panel). The first of these two peaks occurred on the night of December 17, 2012. This peak showed CH_4 enhancement with no corresponding increase in C_2H_6 enhancement, suggesting a biogenic CH_4 source, which was confirmed by the Keeling plot analysis that yielded a source δ^{13}C-CH_4 of -71.55‰ (95% confidence interval: -72.1 to -71.0‰, Fig. 3.7, middle panels). In contrast, the other large CH_4 peak observed during our δ^{13}C-CH_4 measurement period showed co-occurring CH_4 and C_2H_6 enhancement, which would be expected of a thermogenic CH_4 source (Fig. 3.7, bottom left panel). The Keeling plot for this CH_4 peak does indicate a highly enriched potentially thermogenic δ^{13}C-CH_4 value (>-40‰), although the R^2 of the linear fit is low (0.08).

The range of $[CH_4]$ values in our data was insufficient to use Keeling plots to identify the source δ^{13}C-CH_4 of other CH_4 enhancements. In particular, diurnal change in atmospheric δ^{13}C-CH_4 accompanying CH_4 buildup under a stable nocturnal boundary layer has been used to successfully partition CH_4 sources in other urban areas (e.g. London [Lowry et al.; Fisher et al., 2001; 2006], St. Petersburg [Zinchenko et al., 2002], and Krakow [Kuc et al., 2003]). In all of those cases, the nocturnal CH_4 enhancement was large (∼2000 ppb above background), either due to large industrial CH_4 sources (St. Petersburg and Krakow) or local physical

geography (London). However, we found that the nocturnal CH_4 enhancement that we observed in Boston, ∼100 ppb, was insufficient to produce meaningful estimates (i.e. Keeling plot R^2 >0.1) of the nocturnal CH_4 buildup source δ^{13}C-CH_4.

Although the CH_4 enhancements we observed were predominantly from a thermogenic CH_4 source, a small minority of our data had elevated CH_4 enhancement with no corresponding enhancement in C_2H_6, suggesting a biogenic CH_4 source (e.g. Fig 3.3, right panel). We found that these low-C_2H_6 CH_4 plumes came primarily from the direction of the wastewater treatment site ∼15 km from our sampling site (Fig. 3.8). We identified one large CH_4 peak on the night of December 17, 2012 as biogenic based on both the lack of C_2H_6 enhancement and on the depleted δ^{13}C-CH_4 of the source suggested by the Keeling plot (-71.5‰, Fig. 3.7 middle panels). Other biogenic points were identified as those that had Δ-CH_4 enhancement < 2.6 ppb and $\Delta C_2H_6 < 0.026 \cdot \Delta CH_4$ - 2.575 (Fig 3.3, green dots).

To the extent that atmospheric CH_4 enhancement is controlled predominantly by leaks in local infrastructure, it is possible that changes in the leak rate from infrastructure could affect the background atmospheric [CH_4]. Although it is well known among natural gas infrastructure leak surveyors that leakage rates are slightly higher when air pressure is lower (Bob Ackley, Gas Safety USA, personal communication), this connection between urban infrastructure leakage rates and ambient atmospheric conditions has not, to our knowledge, been scientifically examined. Using our smoothed 20th percentile time series as a proxy for background [CH_4], we found that neither air pressure nor temperature was correlated with our [CH_4] data. To investigate whether temperature– or pressure–mediated changes in natural gas infrastructure leakage rates might have a delayed effect on atmospheric [CH_4], we tested for correlations lagged in one-hour increments between 20th percentile [CH_4] and air temperature and pressure, respectively, for time delays of 1 to 72 hours. We found no correlation between atmospheric 20th percentile [CH_4] and either air

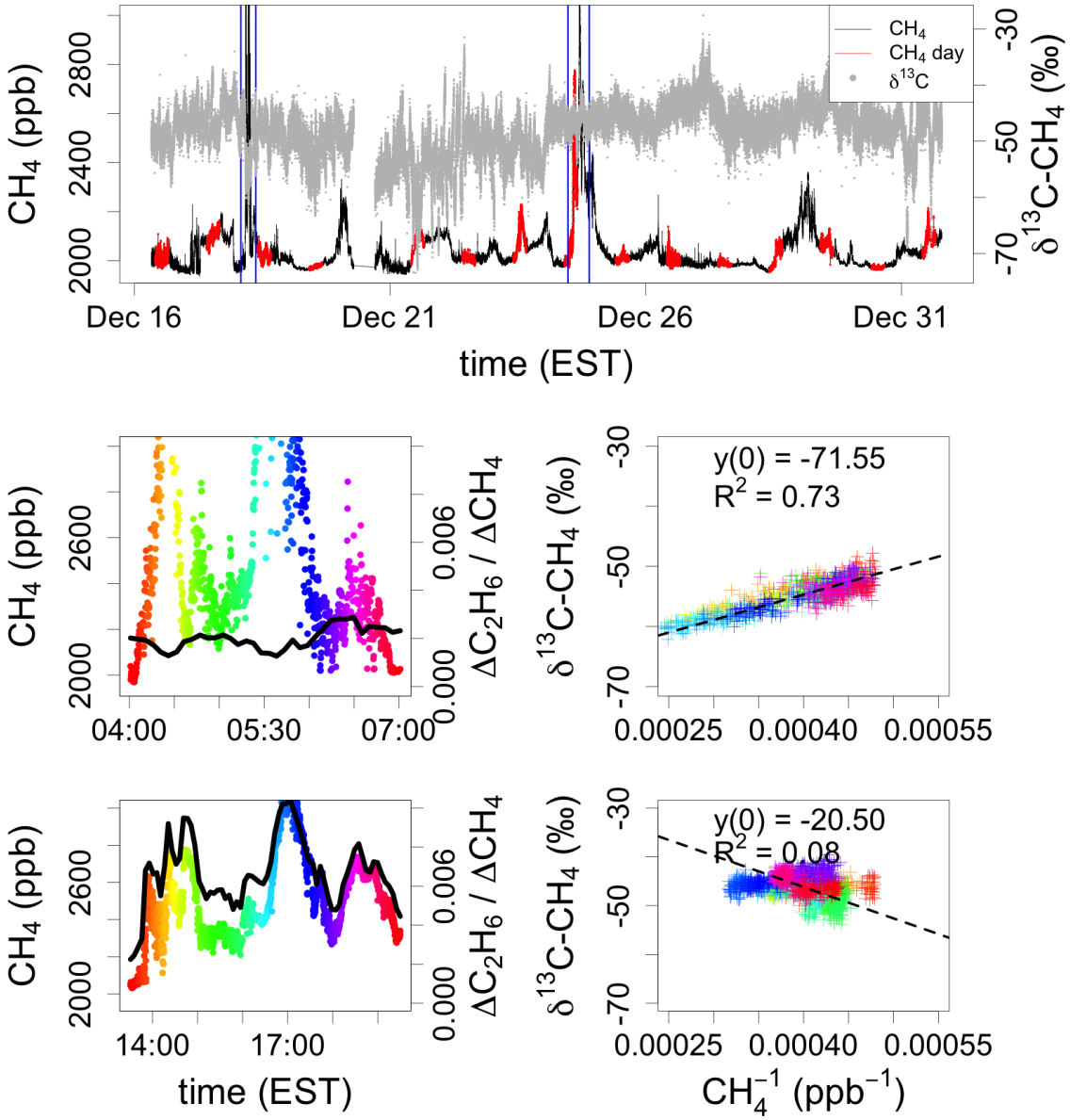

FIGURE 3.7: δ^{13}C-CH_4 values (gray, top panel) of specific peaks further confirm differentiation between thermogenic and biogenic sources. Keeling plots for the two peaks with the largest range in [CH_4] (bounded by blue vertical lines in top panel) are shown in the bottom four panels. Left panels show [CH_4] (left axis, color ramp representing time) and ratio of C_2H_6 enhancement to CH_4 enhancement (right axis, black line) for the two peaks indicated in top panel. Right panels show Keeling plots of δ^{13}C-CH_4 as a function of 1/CH_4 (colors represent time and correspond to left panel), with the MA linear fit (dotted black line). The CH_4 peak observed on the night of Dec. 17, 2012 (middle panels), has little [C_2H_6] enhancement, consistent with a biogenic CH_4 source, and the source δ^{13}C-CH_4 suggested by the Keeling plot is strongly biogenic, -71.55‰ (R^2 = 0.73). The CH_4 peak observed during the day on Dec. 24, 2012 (bottom panels), had simultaneous CH_4 and C_2H_6 enhancements, consistent with a thermogenic source. The source δ^{13}C-CH_4 suggested by the Keeling plot is potentially thermogenic, but the low R^2 of the linear fit makes it difficult to definitively identify a source.

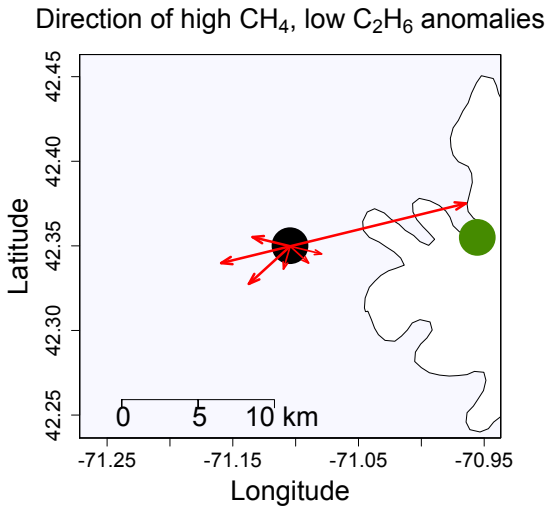

FIGURE 3.8: Direction of origin for points with high [CH_4] and comparatively low [C_2H_6]. Gray area is land, Massachusetts Bay is shown on the right in white. Black dot is the Boston University sampling location and green dot is the largest wastewater treatment facility in the Boston area, ~15 km distant from our sampling site. The majority of the relatively small amount of biological CH_4 enhancement that we observed occurred during periods in which the wind came from the direction of the wastewater treatment facility.

temperature or pressure at any time delay interval. This lack of correlation suggests that either leakage rates from natural gas infrastructure are relatively independent of atmospheric conditions or atmospheric [CH_4] values are controlled more by broader atmospheric transport and meteorological conditions than by local conditions. Further study will be necessary to determine to what extent CH_4 emissions from infrastructure point sources are affected by atmospheric conditions, and whether such changes could impact top-down CH_4 emissions estimates.

3.5 Conclusion

We have presented an algorithm for partitioning urban CH_4 flux between biogenic and thermogenic CH_4 sources based on the [CH_4] and [C_2H_6] measured on a rooftop compared to the [CH_4] and [C_2H_6] signatures of potential CH_4 sources. We find that

88% of the CH_4 enhancement that we observed is due to thermogenic CH_4 sources (95% confidence interval 82–94%). Based on bootstrapping and sensitivity analyses, we conclude that our algorithm is fairly robust against outliers (i.e. high [CH_4] transient peaks). We have used an emissions factor relating Boston's total natural gas delivery to CH_4 leakage to estimate that the city could be emitting 14 g CH_4 per m^2 per year (95% CI: 12–16 g CH_4 per m^2 per year), or 180 Gg (95% CI: 150–210 Gg CH_4 per year).

Leaks in the natural gas distribution infrastructure are a likely source of this urban thermogenic CH_4 enhancement. Past research has shown that leaks from natural gas infrastructure are common in Boston (Phillips et al., 2013) and other cities in the US with aging infrastructure, such as Washington, DC (Jackson et al., 2014). While vehicular traffic is another potential source of thermogenic CH_4 emissions, we found no correlation between the results of our partitioning of CH_4 emissions and the volume of vehicular traffic, which is consistent with other studies that have found that vehicles are not large sources of urban CH_4 (Mays et al., 2009; Townsend-Small et al., 2012).

On a subset of peaks with high [CH_4], Keeling plots of δ^{13}C-CH_4 confirmed the CH_4 source assignment as either biological or thermogenic. However, the diurnal CH_4 fluctuation of ∼100 ppb was insufficient to use changes in δ^{13}C-CH_4 during periods of nocturnal CH_4 buildup as an independent estimator of CH_4 source apportionment.

Although our results suggested that thermogenic sources were responsible for the majority of CH_4 emissions in Boston, we observed a small subset of points with large [CH_4] enhancement with no corresponding increase in [C_2H_6], characteristic of a biological CH_4 source. We found that the majority of these low-C_2H_6 points occurred during periods in which the wind was blowing from the direction of the wastewater treatment facility that is ∼15 km distant from our sampling site.

Our results provide greater insight into the CH_4 emissions for Boston, MA, which

are likely similar to those of other cities in the U.S. and globally that have aging natural gas infrastructure. When combined with forthcoming CH_4 flux estimates from the Boston-area CH_4 monitoring network, our CH_4 source partitioning will help to establish a source-by-source CH_4 budget for the area, which could serve as a starting point for targeted CH_4 emissions reductions measures. Reducing emissions from natural gas infrastructure could be an effective way to reduce overall greenhouse gas emissions from urban areas, while simultaneously reducing ground-level ozone pollution and saving money for consumers and natural gas distribution companies.

Acknowledgement

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4

Pre-drilling background groundwater quality in the Deep River Triassic Basin of central North Carolina, U.S.A.

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4.1 Abstract

Unconventional natural gas development via horizontal drilling and hydraulic fracturing has greatly increased the supply of natural gas in the United States. However, the practice raises concerns about the possibility for impacts on shallow groundwater aquifers. The Deep River Triassic Basin in central North Carolina is likely to contain natural gas that could be extracted via hydraulic fracturing in the future. Unlike other states where hydraulic fracturing has been employed, North Carolina has no history of commercial oil and gas extraction. In this study, we measured water chemistry, dissolved gases, and volatile organic compounds in 51 private drinking water well samples over the Deep River Triassic Basin. Our data document the background water quality of shallow aquifers in the Deep River Basin, which could provide an important baseline dataset if hydraulic fracturing occurs here in the future. We found only two of the 51 water wells sampled had dissolved CH_4 concentrations >0.1 mg/L, and no well had a methane concentration >0.5 mg/L. The δ^{13}C-CH_4 of the two highest CH_4 concentration water wells (-69.5 and -61 ‰) suggest a biogenic CH_4 source and are distinct from the δ^{13}C-CH_4 of two test gas wells drilled in the area (-54.41 and -45.11 ‰). Unlike other basins overlying shale gas formations in the U.S., we find no evidence for CH_4 migration into shallow groundwater in the Triassic basin. In addition, we identified only seven VOCs in five water samples, with levels below the U.S. EPA's maximum contaminant levels. Ion and trace metal concentrations in most samples were also below U.S. EPA primary drinking water standards, with the exception of two samples that exceed the standards for arsenic (As). We modeled the depth of the upper surface of the Cumnock Shale formation in the Deep River Basin using a kriging algorithm and found that its depth below the surface is shallow (0 - ∼1500 m) relative to other shale formations that have been drilled commercially in the U.S., including the Marcellus in Pennsylvania and the Fayetteville in Arkansas.

4.2 Introduction

The combination of horizontal drilling and hydraulic fracturing (HDHF) has dramatically increased the amount of natural gas and oil extracted in the United States and could soon become an important contributor to energy worldwide (Priddle, 2011). These technologies are used to extract hydrocarbons from organic-rich shales and other tight formations that would otherwise be uneconomical to extract. Burning natural gas to produce electricity produces half as much CO_2 as does burning coal (Burnham et al., 2012) but with none of the sulfur dioxides and mercury compounds that are emitted from coal combustion. Although the potential exists for HDHF wells to emit large amounts of uncombusted CH_4 (Howarth et al., 2011), subsequent research has suggested that life-cycle CO_2 emissions from electricity generation using natural gas could be lower than those from coal (Allen et al., 2013; O'Sullivan and Paltsev, 2012; Jiang et al., 2011).

However, concerns have been raised about the potential for hydraulic fracturing to contaminate shallow groundwater supplies. Recent work in the Marcellus Shale basin has demonstrated that water wells within 1 km of hydraulically fractured gas wells had statistically higher dissolved CH_4 and C_2H_6 concentrations on average than those water wells that were not in proximity to a hydraulically fractured gas well (Osborn et al., 2011a; Jackson et al., 2013). While stray gas contamination has been documented in Pennsylvania in some cases, a similar study of private drinking water wells in the Fayetteville shale in Arkansas, U.S.A. found no evidence for shallow groundwater contamination from fugitive gas accompanying HDHF there (Warner et al., 2013a). The geology of the Marcellus Shale area of Pennsylvania is more heavily faulted and fractured than that of the Fayetteville Shale area, and these fractures could provide an avenue for gas and fluid migration in the subsurface (Warner et al., 2012). In this paper, we seek to evaluate the potential for this type of deep fluid

connectivity in the Deep River Basin in North Carolina.

Until August of 2012, horizontal drilling and hydraulic fracturing were illegal in North Carolina. The Deep River Basin in central North Carolina, U.S.A., contains natural gas in the Cumnock Shale formation, which is likely to be drilled using HDHF in the future. Unlike many other areas of the United States with unconventional gas reserves, North Carolina has little or no history of commercial oil and gas extraction. As such, it is important to collect background water quality data in advance of oil and gas drilling. These data will help document changes in water chemistry if hydraulic fracturing occurs in the region.

In this study, we present data from 51 water samples collected from shallow private groundwater wells in the Deep River Basin overlying the Cumnock Shale. This study is, to our knowledge, the first comprehensive effort to document the water chemistry in the Deep River Basin and includes analysis of the distribution of salts, metals, dissolved gases, volatile organic compounds, and isotopic ratios of CH_4 and Sr. This study provides a near-comprehensive water quality database and some insights for the possible hydraulic connectivity between the shale formation and the overlying shallow drinking water aquifer. To further investigate the potential for subsurface fluid migration, we develop a depth model for the Cumnock Shale, with which we are able to identify Cumnock fluids from the shallow, unconfined portion of the shale as containing higher dissolved CH_4 concentrations than those from the overlying Sanford Formation.

4.3 Materials and methods

4.3.1 Geologic setting

The majority of our samples were taken in Lee County, North Carolina, northwest of the town of Sanford, with some samples collected to the north of Lee County in southern Chatham County. The study area is located above the region of the

Cumnock Shale most likely to be drilled for oil and gas first, based on past exploratory drilling and seismic studies (Reid et al., 2011). This area is characterized by gently rolling hills, with the Deep River bisecting the northern portion of the study area (Fig. 4.1). The Cumnock Shale is of Triassic age (∼230 million years old) and is contained within the Deep River rift basin. The Cumnock is underlain by the Pekin sandstone and overlain by the Sanford sandstone formations (see Fig. 4.2). The Deep River basin is divided into three sub-basins: the Sanford, Durham, and Wadesboro. The Durham and Sanford sub-basins are separated by the Colon cross-structure, a constriction of the basin caused by a faulted anticlinal structure (Reid and Milici, 2008). The Wadesboro sub-basin is similarly separated from the Sanford sub-basin by the Pekin cross-structure (Reid and Milici, 2008). The study area is located over the Sanford sub-basin of the Deep River Basin. North Carolina contains another Triassic rift basin, the Dan River Basin, but that area is less likely than the Deep River Basin to contain economically extractable amounts of oil or natural gas (Milici et al., 2012).

The Cumnock Shale is the most likely target of initial gas drilling in North Carolina. The formation ranges in thickness from ∼60 m in the north central area of the basin to 200 m near the Colon cross-structure (Reid and Milici, 2008), sloping downwards towards the southeast, with outcrops at the surface in the northwestern portion of the basin. The Cumnock contains a layer of coal that was mined in the early 1900's (Fig. 4.2). The depth of the Cumnock Shale has not been measured over its entire extent, but the depth model that we developed (see section 3.4 below) suggests that the Cumnock ranges in depth from 0 to ∼1500 m over the study area. The depth to the metamorphic rock underlying the Pekin Formation at the base of the Deep River Triassic basin varies from 0 to ∼1800 m over the study area. Diabase dikes intruded into the Deep River basin during the Late Triassic. These dikes that range in thickness from centimeters to hundreds of meters and in length from meters

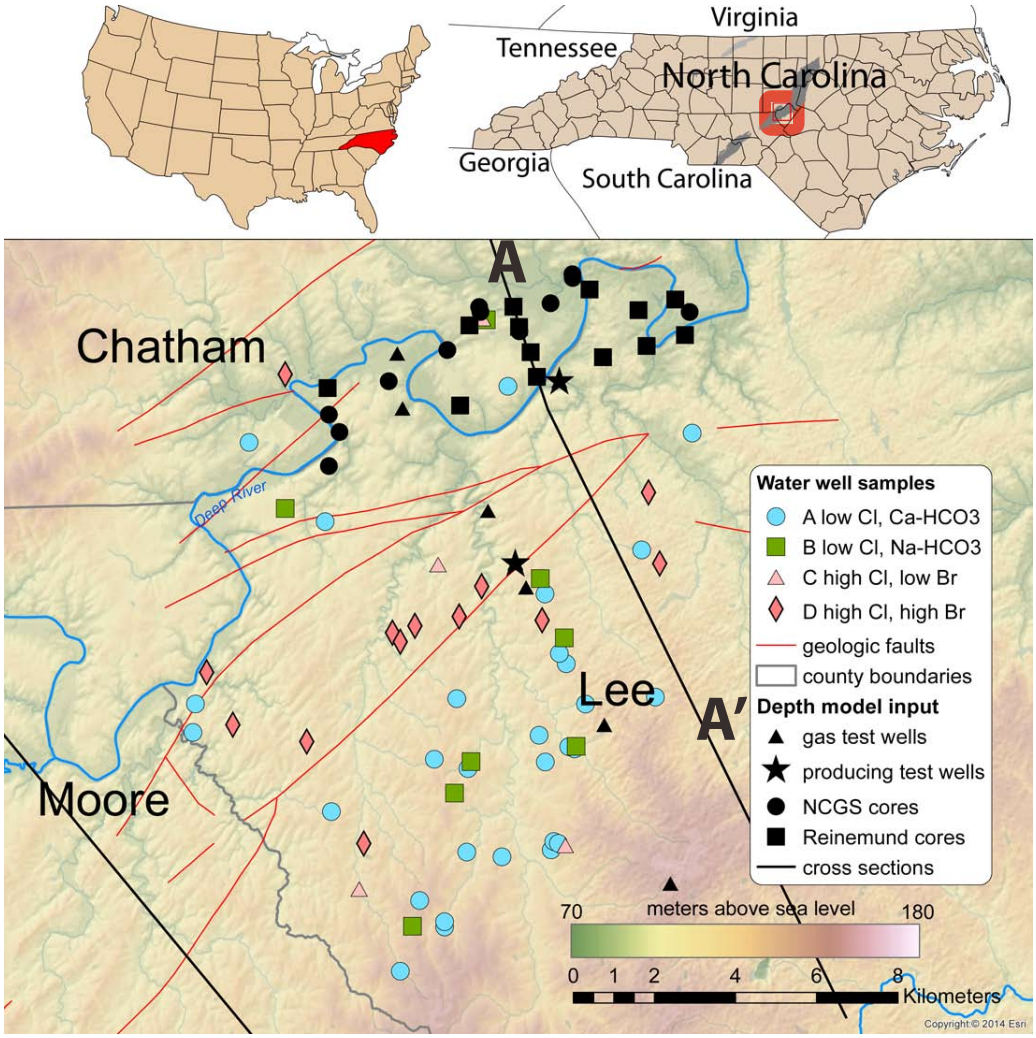

FIGURE 4.1: Location of study area, well water samples, and surface elevation of study area. The Deep River Triassic Basin is highlighted in gray on the state map, with a red box (top right panel) around the inset (lower panel) of the study area that includes portions of Lee, Chatham, and Moore counties. Water well sampling locations are indicated, differentiated by water chemistry types (following Warner et al. (2013a)): Ca-HCO_3 ("type A", blue circles), Na-HCO_3 ("type B", green squares), Cl $>$ 20 mg/L with low Br ("type C", pink triangles), and Cl $>$ 20 mg/L with high Br ("type D", red diamonds). Geologic faults are indicated with red lines. Sources of data used in creating a depth model for the upper surface of the Cumnock Shale are indicated in black symbols, and described in the text. Elevation and fault data are from the NC Geologic Survey. A and A' labels in lower panel refer to the cross section in Fig. 4.2.

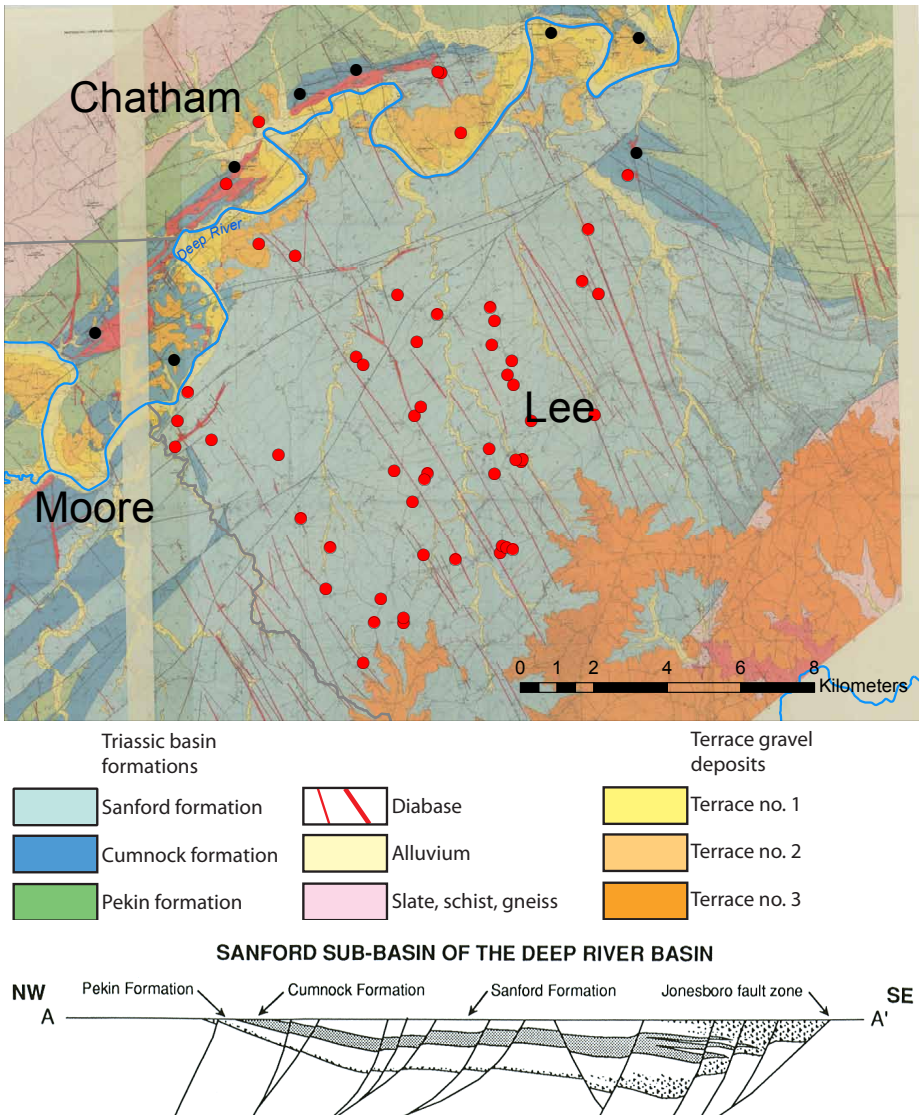

FIGURE 4.2: Surface geology of study area, from Reinemund (1955), with water well sampling locations (red circles), location of former coal mines (black circles), and county labels (black text). Diabase dikes, shown in red, generally run NE to SW, with a large diabase outcrop in the NE of the study area near the border between Lee and Chatham counties. Geologic cross section from the North Carolina Department of Environment and Natural Resources (2012). The Cumnock Shale outcrops in the northwestern portion of the study area (shown in darker blue) and gets deeper towards the southeast.

to kilometers (Reid and Milici, 2008) and generally trend to the northwest, perpendicular to the major faults in the area (Fig. 4.2). The water wells in the Deep River Basin are generally low-yielding when confined to the tight sandstones of the Sanford Formation. However, some wells in the study area, including at least one sampled for this study (as indicated in well construction records), are known to intersect diabase dikes and the Cumnock coal deposits (Reinemund, 1955).

4.3.2 Well water sampling

We collected 51 water samples from private groundwater wells used for drinking water. Well characteristics, including depth, were taken from well construction records provided by the Lee and Chatham County health departments. Where well records were not available, water well information was collected from tags left on the wellhead at the time of construction. Our well water samples were collected between April and August 2012 in collaboration with United States Geological Survey (North Carolina office) personnel. Methods for collection of field parameters, such as pH, temperature, and specific conductance, followed standard USGS protocols (Wilde, 2006). Briefly, water wells were purged until field parameters (temperature, dissolved oxygen, electrical conductivity, and pH) stabilized, and all samples were collected upstream of pressure tanks or filtration devices. Samples collected for trace element and major ion analyses were filtered (0.45 μm) upon collection into 100-ml plastic Nalgene bottles. Samples analyzed for volatile organic compounds were unfiltered and collected in pre-combusted U.S. EPA volatile organic assessment (VOA) vials without headspace. The vials were pre-acidified with 1 mL of 50 % HCl (v/v) for preservation. All samples were preserved on ice in the field subsequently refrigerated at the end of each day of sampling.

Concentrations of major ions, trace metals, and VOCs were analyzed at Duke University. Anion concentrations were determined by ion chromatography and cation

concentrations by direct current plasma optical emission spectrometry (DCP-OES). Trace metal concentrations were determined by VG PlasmaQuad-3 inductively coupled plasma mass-spectrometry (ICP-MS). Alkalinity was determined by titration with HCl to pH 4.5. Dissolved CH_4 concentrations were determined by the USGS CFC lab for all samples (Hinkle et al., 2010). For a subset of samples, dissolved gases were analyzed by Isotech Laboratories for hydrocarbon concentrations and isotopic composition. All carbon isotopes were measured relative to Vienna Pee Dee Belemnite (VPDB). Values of $\delta^{18}O$ and ð of water were determined by thermochemical elemental analysis continuous flow isotope ratio mass spectrometry (TCEA-CFIRMS), using a ThermoFinnigan TCEA and Delta + XL mass spectrometer at the Duke Environmental Stable Isotope Laboratory (DEVIL) and are normalized to Vienna Standard Mean Ocean Water (V-SMOW) and Vienna Standard Light Antarctic Precipitation (V-SLAP), respectively.

All isotopic and Sr concentration analyses were done under clean-lab practices in the Isotope Geochemistry Lab at the University of North Carolina, Chapel Hill. For each water sample, approximately 30 g was weighed and approximately 10 g of ^{84}Sr spike was added. The sample was then dried and subsequently dissolved with 50 µg of 3.5N HNO_3. The samples were passed through ion exchange columns using EiChrom SrSpecTM ion exchange resin. Strontium was isolated from other ions in the sample through rinses with 3.5 N HNO_3 and elution with water. The samples were then dried and loaded onto a rhenium filament and analyzed for Sr concentration and isotopic ratios on a Sector 54 thermal ionization mass spectrometer (TIMS). Samples were run in 3-cycle dynamic mode with an average ion beam intensity of 3V ^{88}Sr with an exponential fractionation correction of $^{86}Sr/^{88}Sr$=0.1194. The resulting $^{87}Sr/^{86}Sr$ ratios were corrected for the molarity of an ^{84}Sr spike added to the sample and re-corrected for fractionation. Replicate analyses of National Bureau of Standards (NBS) reference compound 987 yielded $^{87}Sr/^{86}Sr$ of 0.710258 (NBS reported value

value: 0.71034 ± 0.00026, Moore et al., 1982).

VOCs were quantified by gas chromatography with flame ionization detection (GC-FID) and standard reference compounds: 502.2 CAL 2000 Mega-Mix (no. 30431), 624 Calibration Mix #1 (no. 30020), 624 Calibration Mix #2 (no. 30021), 624 Calibration Mix #3 (no. 30022), all by Restek, Bellefonte, PA, U.S.A. Compounds included in analysis are shown in 4.5. For each water sample, 5-mL aliquots were manually injected with a glass micro-mate syringe (Cadence Science Inc., RI, U.S.A.) into a 5-mL Tekmar glass sparger on a Teledyne Tekmar Stratum Purge and Trap concentrator (Mason, OH, U.S.A.). The sample was purged for 4 minutes with ultra high purity helium, purified again using an RMSH2 purifier (Agilent Big Universal Trap Superior Helium Purifier) at a purge flow of 40 mL/min and dry purged for 1 min at 40°C and 100 mL/min. The sample was then transferred onto an Agilent 7890A GC system with flame ionization detector (FID). The GC column was either an Agilent DB-624 (flow: 6 mL/min; temperature program: 40°C, 2 min hold, ramp 4°C /min to 150°C, then ramp 8°C/min to 200°C) or a Restek-502.2 (flow: 20 mL/min; temperature program: 40°C, 6 min hold, ramp 6°C /min to 200°C). Both are long columns containing hydrophobic, thick stationary phases designed to maximize resolution for volatile hydrocarbons, and calibration standards were used to independently confirm retention times on each column. The compound identities were reconfirmed by GC-MS measurements on an Agilent 7890A GC system with MS 5975C with Chemstation Software.

4.3.3 Historical gas well records

Boreholes and test wells (32) were drilled in the sampling region over the past 50 years to evaluate the potential for oil and gas development. We used information from these wells and from other sources to estimate the depth between the land surface and the top of the Cumnock Shale formation to create a depth model for

the upper boundary of the Cumnock Shale (see section 4.3.4). Two test wells, both drilled in 1998, produced elevated pressure from natural gas and were then capped. Gas samples from these two test wells were collected by the NC Geologic Survey in 2009 and analyzed for gas composition by Isotech Laboratories (Reid et al., 2011).

4.3.4 Depth model

As the Cumnock is relatively shallow in the northern and western portion of the study area, some of the water wells sampled in this study intersect and draw water from both the Cumnock and the overlying Sanford formations. In order to identify which water wells in our study might represent the geochemical signature of fluids from the Cumnock Formation, we reconstructed the depth of the shale. Although the water wells in this study draw from the unconfined portion of the shale, which is influenced by meteoric recharge, we used our depth reconstruction to search for a distinct chemical signature of the shallow portion of the Cumnock Shale. This information could be useful in tracking potential future fluid migration associated with HDHF or predicting the composition of fluids that return to the surface after HDHF(produced water) in the Cumnock.

The depth from land surface to the top of the Cumnock Shale was recorded in well logs of 19 test wells drilled between 1944 and 1998 (Melinda Chapman, United States Geological Survey [Raleigh, NC], personal communication). Reinemund (Reinemund, 1955) also documented depth from land surface to upper shale boundary in 13 deep wells in the northwestern portion of the study area. Our depth estimate was constrained at these 32 points and along known boundaries of Cumnock surface outcrops (Fig. 4.2). The model was further constrained along two depth transects presented in Reinemund (Fig. 4.1). Since the depth to shale changes discontinuously at fault boundaries, each area bounded by faults was modeled independently.

Using these data, the depth of the surface of the shale was estimated via an

ordinary kriging approach (Ahmadi and Sedghamiz, 2008). A cubic semivariogram was employed to minimize the uncertainty over the relatively large and sparsely documented area of the depth surface (Nikroo et al., 2010). The parameters of the semivariogram were determined by an iterative least squares fit. The resulting kriged surface is shown in Fig. 4.3 and varies in depth from 0 in the northwest of the study area to ∼1500 m below ground level in the southwest. The standard deviation of the kriged depth estimate is shown in Fig. 4.3 and ranges from <100 m in the northern portion of the study area, with the highest density of depth measurements, to >500 m in the south-central portion of the study area, where there are no measured shale depth points to constrain the model.

4.4 Results and discussion

4.4.1 Geochemical and depth characterization

Shallow groundwater samples were divided into four water categories based on major water chemistry (following the framework of Warner et al. (2013a)). Samples with < 20 mg/L of Cl were divided based on whether they were dominated by Ca (defined as "type A", n = 29) or Na ("type B", n = 8) waters. The Ca-HCO_3 water type represents interaction with calcium carbonate minerals in the aquifer. The difference between Ca-HCO_3 and Na-HCO_3 water types could indicate different rock sources and/or a longer residence time in groundwater with a longer flow path and exchange with clay minerals (Warner et al., 2013a). Samples with > 20 mg/L of Cl were divided based on Br/Cl ratios: those with Br/Cl < 0.0015 ("type C", n = 3) and those with Br/Cl > 0.0015 ("type D", n = 13). The elevated [Cl] with low Br/Cl represented by type C waters could be indicative of anthropogenic surface contamination, such as leaching from septic fields. In contrast, the elevated Cl and Br in type D waters are consistent with the Br/Cl ratio of evaporated seawater (Fig. 4.4, McCaffrey et al. (1987)). The presence of saline groundwater with a Br/Cl ratio above that of

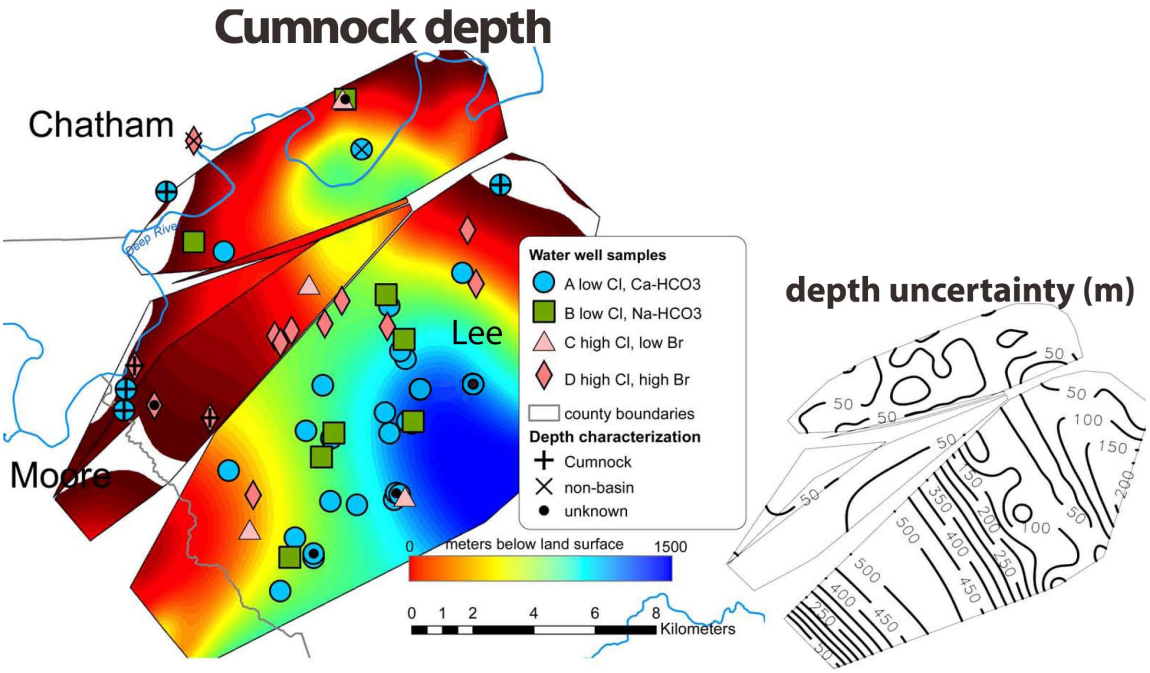

FIGURE 4.3: Inferred depth of Cumnock Formation within study area, based on data sources pictured in Fig. 4.1 and described in the text. The shale ranges in depth from near surface (red) to 1500+ m (blue). Discontinuous changes in shale depth occur at faults. Each zone bounded by faults was modeled independently using ordinary kriging with a cubic semivariance function. Shape and color of symbols represent water chemistry of sampled water wells and follows Fig. 4.1. The depth model was used to identify which water wells intersect the Cumnock (black cross, n = 6) and those that do not. Wells in terrace gravel deposits were classified as "non-basin" (black x, n = 2). Wells for which depth data is not available are labeled "unknown" (black dot, n = 5). Uncertainty in depth estimate (standard deviation) is shown in right panel.

seawater has been interpreted as an indicator for mixing with deep saline water in other areas (Warner et al., 2012). Although the 20 mg/L Cl threshold employed by Warner was motivated by the distribution of Cl concentrations in historical groundwater records of northwestern Pennsylvania, it is employed here because there is, to our knowledge, no pre-existing Cl concentration data for the Triassic Basin upon which to revise this threshold to the Triassic Basin aquifer.

Water wells were also classified based on the depth of their screened interval in relation to the reconstructed Cumnock Shale depth (Fig. 4.3). Wells that intersected

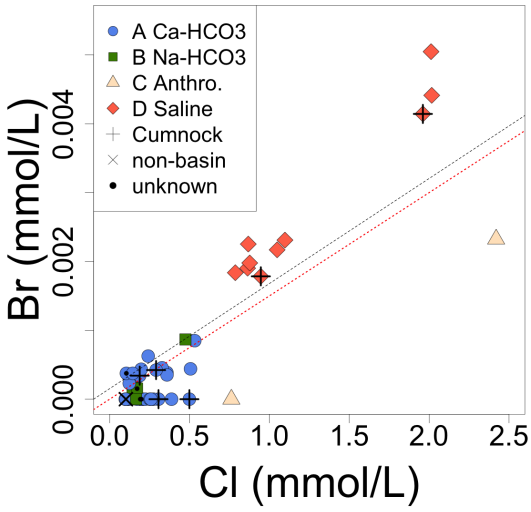

FIGURE 4.4: Br and Cl concentrations measured in shallow groundwater samples. Br and Cl were correlated (R^2=0.673), and the line of best fit (dotted, black) very nearly follows the seawater evaporation line (dotted, red).

the upper boundary were classified as "Cumnock wells" (n = 6). All Cumnock wells were either within Cumnock outcrops or were cased through the predicted depth of the overlying Sanford Formation. Wells that did not intersect the top surface of the Cumnock were classified as "Sanford wells" (n = 38). Wells that were outside of the Triassic basin were classified as "non-basin wells" (n = 2). Wells for which no depth information was available were labeled as "unknown" (n = 5).

4.4.2 Water quality

Ca^{2+} and Na^{+} were the dominant cations in all samples, with no sample having more than 0.4 MEQ % Mg (Fig. 4.5). HCO_3^{-} was the dominant anion in most of our well water samples. SO_4^{2-} was the dominant anion in only three samples, with more than 0.35 MEQ %. These samples were also high in Cl and low in Br, further suggesting that water defined as type C originated from anthropogenic contamination (Office of Water, 1999).

Variations in $\delta^{18}O$ and ð in our samples are consistent with the Local Meteoric

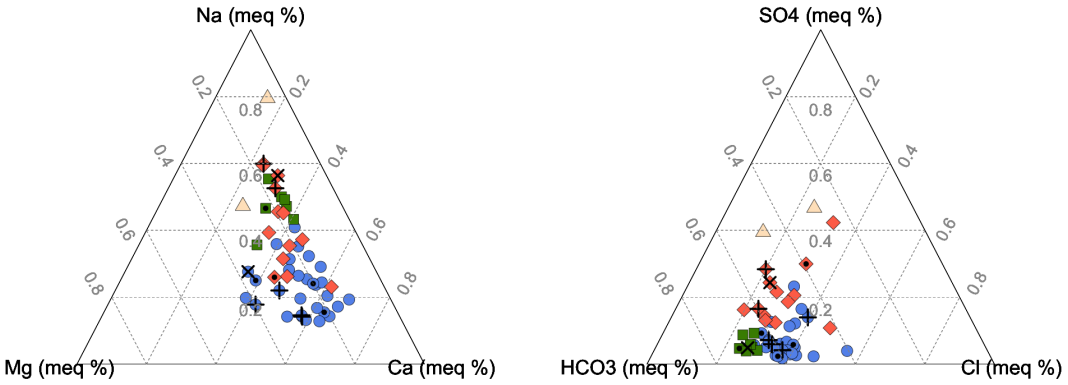

FIGURE 4.5: Major cations (left panel) and anions (right panel). Symbols follow those in figure 4.3.

Water Line (LMWL) (Kendall and Coplen, 2001) (Fig. 4.6), which suggests that samples were influenced by modern precipitation and that subsequent changes in water chemistry were caused by water-rock interactions. Mixing with saline fluids confined within the Cumnock Shale could cause salinization of the fresh meteoric water and increase the $\delta^{18}O$ and ð values. The chemistry and stable isotope composition of the study groundwater indicate that the shallow aquifers are replenished by active recharge of meteoric water with contributions from other water types in the area, such as Na-HCO_3 water (type B), anthropogenically contaminated water (type C), and mixed saline water (type D). The Cumnock wells identified in this study are relatively shallow and draw from the unconfined zone of the shale and did not show evidence of a strongly saline signature. We conclude that, in the unconfined and shallow area of the Cumnock Formation, the groundwater is dominated by meteoric water.

Distributions of some of the inorganic constituents are illustrated in Fig. 4.7. Of the 51 water wells measured in this study, 21 exceeded U.S. federal or NC state

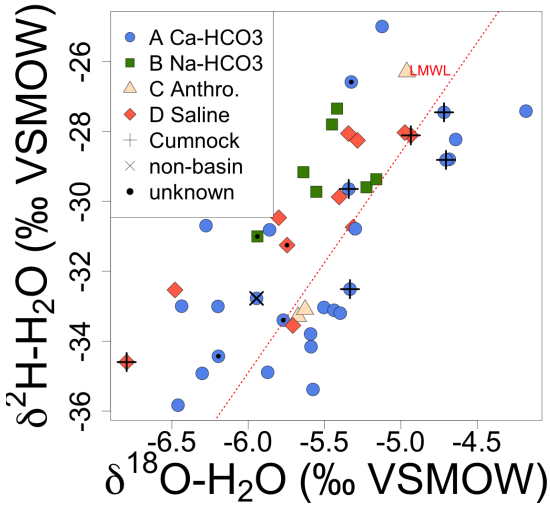

FIGURE 4.6: Isotopes of oxygen and hydrogen in water samples follow the local meteoric water line (LMWL), suggesting a relatively recent meteoric source and short residence time underground.

drinking water standards for at least one element, all shown in Fig. 4.7. The U.S. Environmental Protection Agency (EPA) establishes legally enforceable primary water quality standards to limit the levels of contaminants in drinking water. Only two wells exceeded a U.S. EPA primary water quality standard, both for As. Unlike primary water quality standards, U.S. EPA's secondary water quality standards are not legally enforceable and regulate contaminants that may cause aesthetic effects, such as taste, odor, or color. Of the 21 samples exceeding water quality standards, 16 exceeded the EPA secondary standard for Mn of 50 µg/L. The one sample that exceeded the EPA secondary standard for Cl (250 mg/L) was a notable outlier, with almost 3 times the Cl of any other sample in this study. This type C sample near the center of our study area had notably high concentrations of a number of other elements, including Li, Na, Mg, Cl, Ca, Mn, Br, and Sr, possibly due to local anthropogenic contamination.

There are eight former coal mines in the study area, mostly located towards

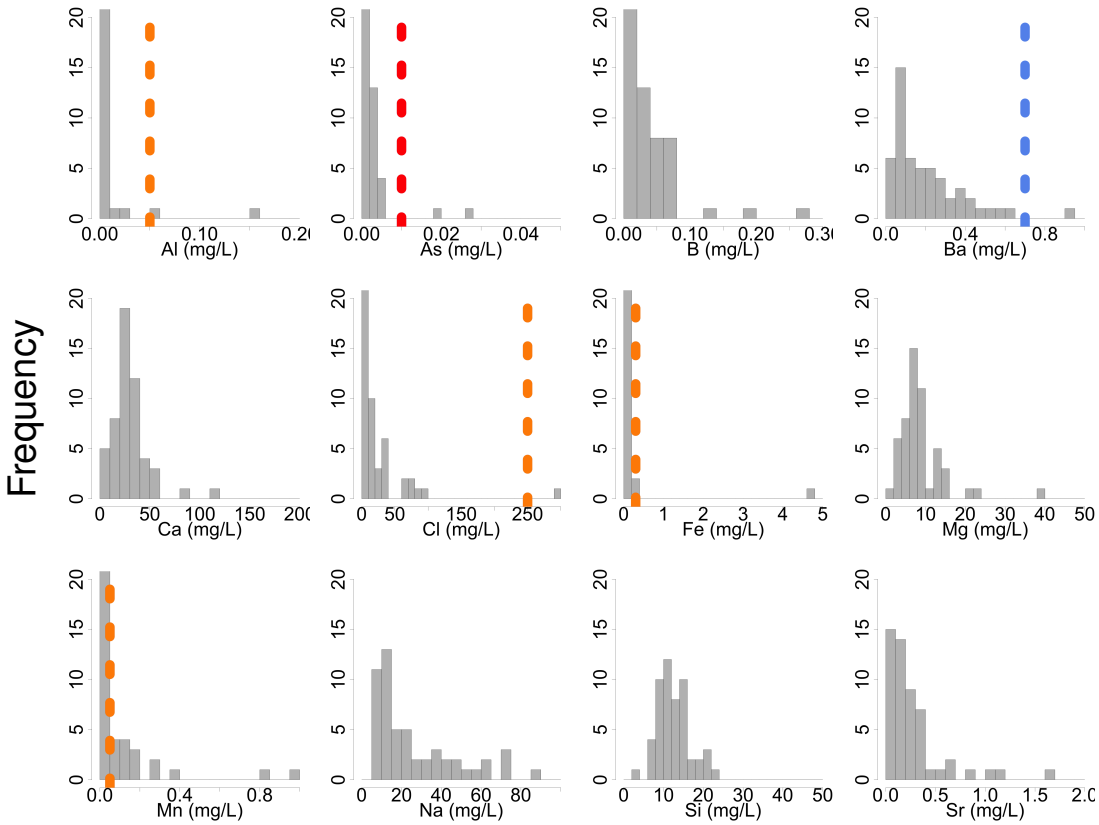

FIGURE 4.7: Distribution of concentrations of a subset of elements measured in this study. Water quality standards are shown as dotted lines: U.S. EPA primary standards in red (As only), U.S. EPA secondary standards in orange (Al, Cl, Fe, and Mn), and NC primary standards in blue (Ba only). For panels with no water quality standards shown, there are either no existing water quality standards for that element (Ca, Mg, Na, Si, Sr) or all federal and state water quality standards exceed the range of values we measured (B). Few concentrations exceeded any federal or state water quality standards. Only two detections exceeded a national primary drinking water standard, both for As. More wells in this study exceeded the Mn secondary standard of 50 µg/L than any other drinking water standard.

the north and west parts of the basin where the Cumnock outcrops at the surface (Fig. 4.2). We expected water-rock interactions with the coal to produce elevated Na in water samples taken near former coal mines (Cheung et al., 2010). However, we found no systematic trend towards Na-HCO_3 type B waters in the northern part of the study area (Fig.4.1).

The Sr isotopic composition, $^{87}Sr/^{86}Sr$, varied from 0.709 to 0.713 (Fig. 4.8) and showed no significant difference between the different water chemistry groups or the locations of wells in different geological formations. Sr isotope ratios also showed no correlation with major element concentrations, including B and Cl. However, 7 of the 8 lowest Sr isotope ratios were measured in groundwater samples from the northern portion of the study area near the Deep River. One possible source for this preferentially low Sr isotopic ratio in the northern portion of the study is groundwater interactions with the large number and volume of diabase intrusions in this area. The $^{87}Sr/^{86}Sr$ ratios of the diabase in the Deep River Basin are between 0.7044 and 0.7072 (Pegram, 1990). Thus, Sr input from these diabase formations could lower the Sr isotopic ratios in groundwater that has interacted with diabase rocks. However, although there are numerous diabase dikes in the northern portion of our study area, these dikes occur in other parts of our study area as well. Moreover, the diabase formations in the Deep River Basin are dominated by olivine tholeiite, with 8.80 15.14% MgO (Pegram, 1990), but we see no correlation between Sr isotopic composition and Mg concentration in groundwater samples (Fig. 4.8). Surface water input is another possible source of the relatively lower $^{87}Sr/^{86}Sr$ ratios in groundwater from the northern portion of our study area. Rainwater in the Deep River Basin has an isotopic range of 0.7087 to 0.7107 (Tanner and Coleman, in preparation). Thus, mixing with surface water could produce groundwater samples with relatively low [Sr] and $^{87}Sr/^{86}Sr$. However, we did not find any correlation between [Sr] and $^{87}Sr/^{86}Sr$, nor do elements other than Sr show evidence of enhanced surface water interaction in the lowest $^{87}Sr/^{86}Sr$ samples. Thus, determining the source of the geographic pattern of Sr isotopic composition that we observed will likely require further study.

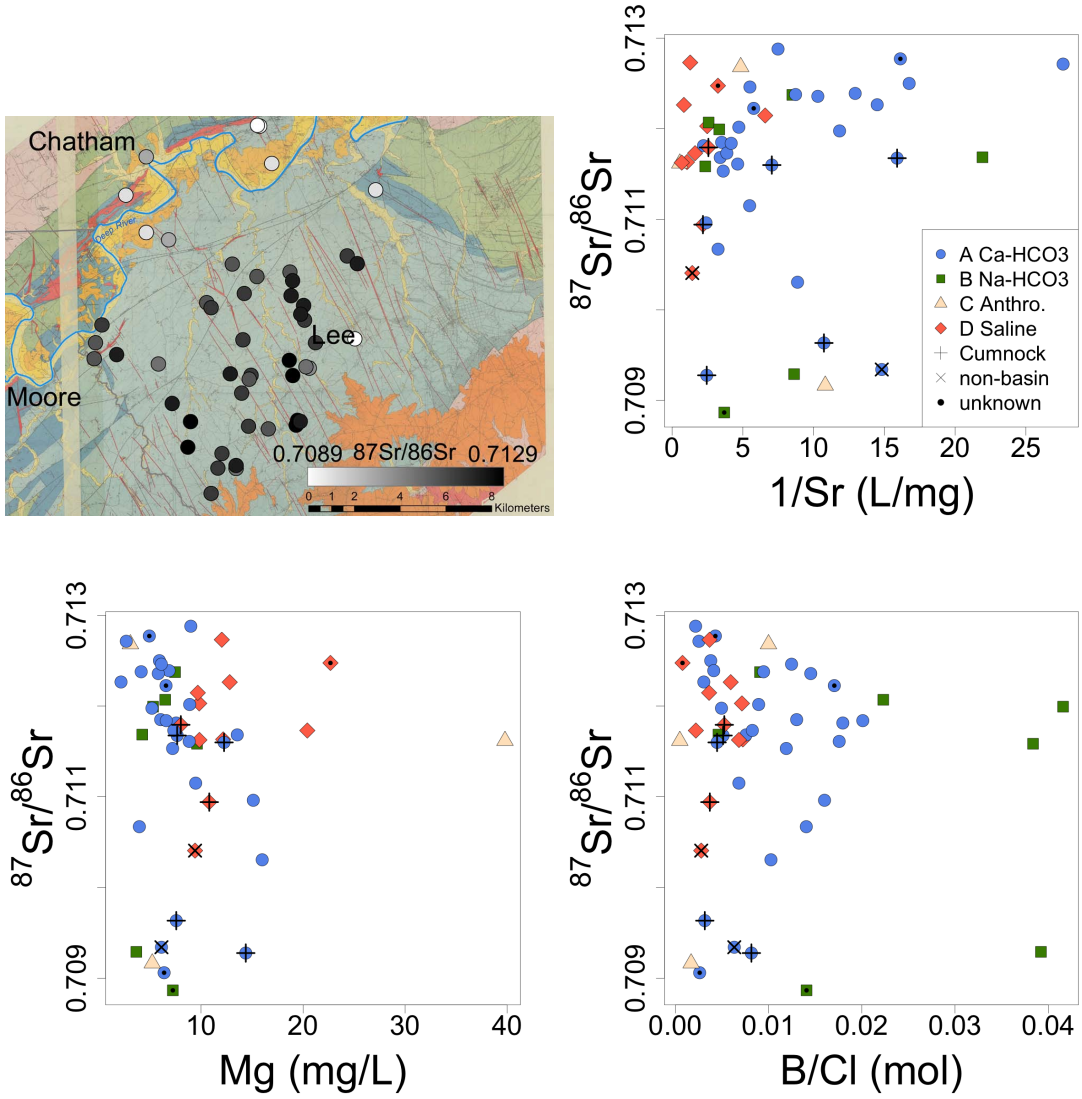

FIGURE 4.8: All water samples with $^{87}Sr/^{86}Sr < 0.710$ except for one occurred in the northern portion of the study area (top left panel). One possible explanation for this distribution is the large concentration of diabase dikes in the northwest of the study area. However, Sr isotopes showed little correlation with Mg (lower left panel), which would be expected from interactions with dikes rich in olivine tholeiite. Infiltration of low $^{87}Sr/^{86}Sr$ surface water near the Deep River in the northern portion of the study area could also cause the low Sr isotopic ratios observed in groundwater samples. However, ions other than Sr did not show evidence for extensive surface water infiltration, and Sr isotopes showed little correlation with most ions (Sr and B shown in right two panels). Based on our data, it is difficult to determine the mechanism controlling the geographic distribution of $^{87}Sr/^{86}Sr$ in the Deep River Basin.

4.4.3 Methane

We detected dissolved CH_4 (> 0.001 mg/L) in 25 of the 51 samples analyzed (Fig. 4.9). Of the 25 samples with detectable CH_4, only two had dissolved CH_4 concentration > 0.1 mg/L: 0.24 and 0.48 mg/L, allowing for isotopic analysis, and both were from Cumnock wells. Cumnock water samples had statistically higher CH_4 concentration on average ($P < 0.01$) than samples from either the Sanford Formation or from outside the Triassic basin. Overall, the CH_4 concentrations in background drinking water samples in NC were much lower than those measured in areas above the Marcellus shale (Heisig and Scott, 2013), somewhat lower than those measured above the Fayetteville shale (Warner et al., 2013a), and well below the 10 mg/L action level recommend by the U.S. Department of the Interior (Eltschlager et al., 2001).

There are multiple lines of evidence suggesting that the CH_4 in the two highest-CH_4 water samples was formed biologically. Both the $\delta^{13}C$ of CH_4 and the ratio of CH_4 to higher chain hydrocarbons, such as C_2H_6 and C_3H_8, can be used to differentiate CH_4 formed biologically from thermogenic CH_4 (Schoell, 1980). Biological CH_4 production, such as anaerobic fermentation and bacterial carbonate reduction, generally give rise to CH_4 that is depleted in ^{13}C, with $\delta^{13}C$-CH_4 between -80 ‰ and -60 ‰ (Whiticar, 1999). Thermogenic CH_4 formation typically results in less fractionation of the end product, with $\delta^{13}C$-CH_4 of produced CH_4 greater than -40 ‰ (Schoell, 1980). Higher chain hydrocarbons such as C_2H_6 and C_3H_8 are commonly formed along with CH_4 during thermogenic CH_4 production, but CH_4 is the only hydrocarbon produced in measurable quantities by biological reactions on land (Schoell, 1980).

The $\delta^{13}C$-CH_4 values measured from the two highest-CH_4 water well samples were -69.5 ‰ and -61 ‰, both suggesting a biological CH_4 source (Fig. 4.10 and table 4.1). No higher-chain hydrocarbons were detected in either of the highest-CH_4

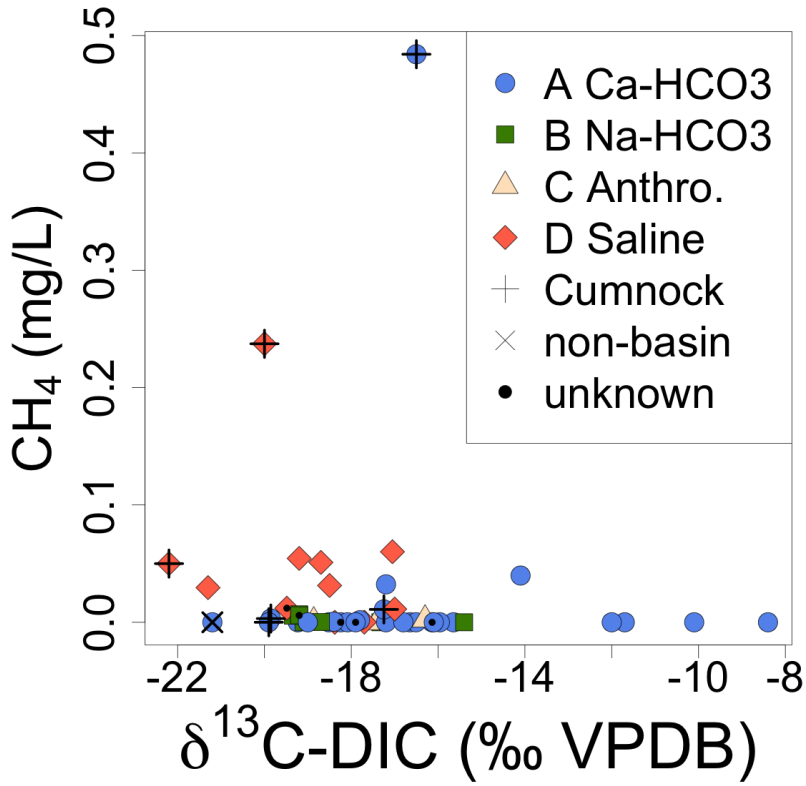

FIGURE 4.9: CH_4 concentration and δ^{13}C-DIC of shallow groundwater samples. All but two water samples had [CH_4] < 0.1 mg/L. Type D samples, with Cl > 20 mg/L and elevated Br, had statistically higher [CH_4] than other types of samples. The δ^{13}C-DIC of water samples was similar to that of source organic matter ($\sim$ -22 ‰), with no evidence for fractionation associated with thermogenic CH_4 modification.

water samples (detection limit 0.1 mg/L), also indicative of a biological CH_4 source. These δ^{13}C and higher-chain hydrocarbon values contrast with those measured in samples taken from two test gas wells drilled in the region. CH_4 samples from these two test gas wells had δ^{13}C of -45.11 ‰ and -54.41 ‰, indicative of a thermogenic and possibly mixed thermogenic and biogenic source. C_2H_6 and C_3H_8 were detected in both of the gas well samples (table 4.1), but none of the highest-concentration CH_4 water samples, further suggesting a biogenic source for the CH_4 detected in these water samples. There is no evidence of thermogenic CH_4 migration from the Cumnock

Shale into overlying aquifers at the present. This is in contrast to the CH_4 migration into shallow groundwater documented in the Marcellus Shale in northeastern PA (Warner et al., 2012).

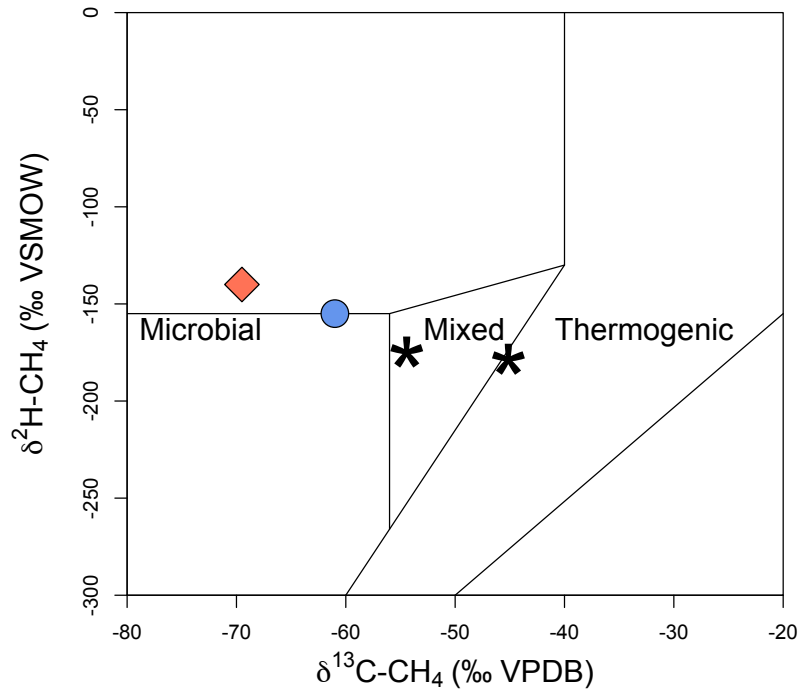

FIGURE 4.10: δ^{13}C-CH_4 and ð-CH_4 of two well water samples with $[CH_4] > 0.1$ mg/L (red diamond and blue circle, indicating type D and type A waters respectively; both highest-CH_4 samples are from the Cumnock Formation) and two test gas wells drilled in to the Cumnock shale within the study area. Classification regions follow Schoell and others (Schoell, 1980; Whiticar, 1999; Jackson et al., 2013). CH_4 in water well samples appears to be produced microbially and not due to migration of thermogenic CH_4 from the Cumnock formation.

Bulk water chemistry types were correlated with CH_4 concentration in our water samples, where type D waters (with high Cl and Br) had elevated CH_4 levels. The co-occurrence of slightly saline water and CH_4 suggests a flow of CH_4-rich groundwater from deep sources, as was observed in groundwater overlying the Marcellus shale in

Table 4.1: Hydrocarbon concentration and isotopes for methane (C1), ethane (C2), and propane (C3) in two highest-CH_4 concentration well water samples and two test gas wells in the study area. Dash symbol ("-") indicates concentration below detection limit for isotopic analysis.

sample	**C1/C+**	δ^{13}**C-C1**	**ð-C1**	δ^{13}**C-C2**	**ð-C2**	δ^{13}**C-C3**	**ð-C3**
water wells							
NCL-08	–	-69.5	-140	–	–	–	–
NCL-17	–	-61.0	-155	–	–	–	–
gas wells							
Simpson # 1	19.82	-54.41	-174.8	-34.60	-151.4	-29.66	-120.6
Butler #3	9.04	-45.11	-178.5	-36.81	-175.8	-31.61	-121.3

northeastern PA (Vengosh et al., 2014). Here, the CH_4 concentration was too low in all but the two highest-CH_4 water samples to analyze the δ^{13}C-CH_4 and C_2H_6 concentrations to determine the CH_4 source. As such, it is not possible to determine whether the detected CH_4 observed in type D waters is due to mixing with deeper saline water containing thermogenic CH_4 or more shallow biogenic CH_4. The mixed thermogenic-biogenic composition of the two production gas wells in the Cumnock could reflect the early stage of maturation of the natural gas relative to natural gas from other shale formations with more thermogenic signatures (i.e. δ^{13}C-CH_4 > -50 ‰), such as the Marcellus Shale (Osborn et al., 2011a). Nonetheless, the isotopic fingerprint of the Cumnock Shale gas presented in this study can be used to identify fugitive gas contamination in the study area if it occurs in the future.

Although δ^{13}C-CH_4 data are not available for water samples with CH_4 < 0.1 mg/L, the C isotopes of dissolved inorganic carbon (DIC) can provide some indirect insight into the mechanisms governing CH_4 formation (Fig. 4.9). The two primary sources of DIC in most groundwater environments are dissociation of CO_2 from the decay of organic matter in the soil during the recharge process, with a δ^{13}C of approximately -23 ‰ (Aravena et al., 1992), and C from the dissolution of marine carbonate rocks, with δ^{13}C of around 0 ‰ (Sharma et al., 2013). In our data, the

mean δ^{13}C-DIC of samples with detectable CH_4 (-18.43 ‰) was slightly more negative than that of samples without detectable CH_4 (-16.52 ‰, $P < 0.05$). Average DIC was also significantly different between water types ($P < 0.05$), with type D waters having the lowest group mean value of -18.9 mg/L ($P < 0.1$, ANOVA post-hoc test with Bonferroni adjustment). The δ^{13}C-DIC of the shallow groundwater samples in our study was close to the -23 ‰, which suggests that most of the DIC was derived from degradation of organic matter and likely rules out possible fractionation associated with CH_4 modification.

Na-HCO_3 type B water samples did not exhibit higher CH_4 concentrations on average than Ca-HCO_3 type A water samples. In studies of water samples from other shale basins (Warner et al., 2013a; Molofsky et al., 2013), the longer residence time of Na-HCO_3 waters relative to Ca-HCO_3 generally gives rise to statistically significant enhancements in CH_4 concentration in Na-HCO_3 waters relative to Ca-HCO_3 waters. The lack of CH_4 enrichment in type B waters is further evidence for a lack of widespread CH_4 migration from the Cumnock Shale into overlying aquifers.

Elevation has been suggested as a controlling factor for CH_4 concentration in groundwater in the Marcellus Shale region of Pennsylvania (Molofsky et al., 2013). However, our study area has little variation in surface elevation (∼70 - 180 m above sea level), and elevation is not well correlated to CH_4 concentration ($R^2 = 0.052$). Furthermore, elevation does not appear to strongly influence water chemistry, as sample types (A through D) are not statistically distinguishable as a function of surface elevation using ANOVA.

4.4.4 Volatile organic compounds

VOC loads in shallow groundwater were generally low and do not appear to be correlated with geologic formation or water type (table 4.2). We detected select VOCs (e.g. chloroform, toluene, and ethylbenzene) above detection limits (in 5 of

51 samples) (table 4.2), and none exceeded EPA maximum contaminant levels.

The halogenated VOCs detected (table 4.2) have known industrial sources; for example, chlorinated ethanes from the breakdown of trichloroethylene; 1,3-dichlorobenzene as an intermediate of the chemical industry; ethylbenzene and toluene as petroleum components; and chlorinated compounds used as solvents (except chloroform, which can be formed naturally, but not at milligram per liter concentrations). Further, the detected compounds are not typically present in agricultural chemicals that could be in use in the rural study area, such as pesticides and fertilizers. We were not able to locate other common potential industrial sources, such as army bases or dry-cleaning businesses, within our study area (using Google Maps), except for the presence of an automotive repair shop. Vengosh et al. (2014) hypothesized that halogenated light hydrocarbons could form in highly saline, CH_4-rich shales, under high temperatures and pressures. While the natural formation of these compounds has yet to be demonstrated, the Cumnock is relatively shallow formation and it is unclear whether the temperature and pressure within the formation are sufficient to form halogenated VOCs directly. Thus, we postulate that the VOCs observed in this well were most likely the result of a local anthropogenic source.

4.5 Conclusions

We have presented, to our knowledge, the first comprehensive evaluation of the water chemistry and dissolved gas in the Sanford sub-basin of central North Carolina. Of the 51 sampled private drinking water wells, we found the majority did not exceed federal or state drinking water quality standards. Only two wells exceeded a U.S. EPA primary drinking water standard, both for As. Of the 51 wells sampled in this study, 16 exceeded the U.S. EPA secondary drinking water standard for Mn, with two wells simultaneously exceeding the secondary standard for Fe and one well for Cl. Volatile organic compounds are largely absent from shallow groundwater in the

area. This is to be expected, as this area has no history of heavy industry or other source of organic compound contamination.

We have used data from research wells and test gas wells to reconstruct the depth of the surface of the Cumnock Shale (Fig. 4.3). The upper surface of the Cumnock Shale is distributed between 0 and ∼1500 m below the surface within our study area, which is much shallower than the depth of other shale deposits, such as the Marcellus Shale in Pennsylvania or the Fayetteville Shale in Arkansas.

We found relatively low dissolved CH_4, with only two samples having CH_4 concentrations above 0.1 mg/L. Based on their low δ^{13}C-CH_4, these two samples appear to be from biogenic sources and are not consistent with the isotopic and higher-chain hydrocarbon signature of natural gas observed in test wells from the Cumnock Shale. We found no evidence for migration of thermogenic CH_4 from the Cumnock Shale into shallow aquifers over geologic time. This current lack of CH_4 in groundwater could serve as an important comparison if HDHF occurs in this area in the future.

Acknowledgements

This research was supported by a grant from the Water Resources Research Institute of North Carolina. We wish to thank Melinda Chapman and the field technicians at the North Carolina office of the U.S. Geological Survey who were instrumental in gathering well construction records and developing contacts with homeowners. We would like to thank Jon Karr of the Duke Environmental Stable Isotope Laboratory for laboratory analysis and Alissa White and Alison Vo for assistance with field sampling and laboratory analysis.

Appendix 4A: Volatile organic compound detections

Table 4.2: Volatile organic compounds detected in water well samples. All measurements, limits of quantification (LOQ), and maximum contaminant levels (MCL) in terms of ng/L. All detections fell below EPA maximum contaminant levels. VOC detections showed no correlation with water chemistry or water well geologic formation.

Sample ID	8	10	21	28	46	LOQ	EPA MCL
Water type	D	B	A	D	A		
Geologic formation	Cu.	Sanf.	unkn.	Sanf.	Sanf.		
chloroform			480			4000	70000
toluene		9		1020		1000	320000
1,1,2-trichloroethane	140					4000	80000
dibromochloromethane	770					10000	60000
ethylbenzene	65					400	700000
1,3-dichlorobenzene	55	20				400	1000000
trichloroethene					1550	4000	5000

Appendix 4B: Volatile organic compound standards

Compound	LOQ (µg/L)
chloromethane	100
vinyl chloride	50
methanol	50
bromomethane	50
chloroethane	50
trichlorofluoromethane	100
1,1-dichloroethene	4
methylene chloride	4
trans-1,2-dichloroethene	10
1,1-dichloroethane	4
2,2-dichloropropane	8
cis-1,2-dichloroethene	8
chloroform	4
bromochloromethane	4
1,1,1-trichloroethane	4
1,1-dichloropropene	4
carbon tetrachloride	40
1,2-dichloroethane	4
benzene	1
trichloroethene	4
1,2-dichloropropane	4
bromodichloromethane	4
dibromomethane	4
cis-1,3-dichloropropene	4
toluene	1
trans-1,3-dichloropropene	4
1,1,2-trichloroethane	4
1,3-dichloropropane	4
tetrachloroethene	4
dibromochloromethane	10

Compound	LOQ (µg/L)
1,2-dibromoethane (EDB)	4
chlorobenzene	1
ethylbenzene	1
1,1,1,2-tetrachloroethane	4
m-xylene	20
p-xylene	20
o-xylene	20
styrene	20
bromoform	1
1,1,2,2-tetrachloroethane	4
1,2,3-trichloropropane	4
n-proplbnezene	10
bromobenzene	4
1,3,5-trimethylbenzene	4
2-chlorotoluene	10
4-chlorotoluene	4
1,2,4-trimethylbenzene	4
sec-butylbenzene	4
4-isopropyltoluene (p-cymene)	4
1,3-dichlorobenzene	1
1,4-dichlorobenzene	1
n-butylbenzene	4
tert-butylbenzene	4
1,2-dichlorobenzene	1
1,2-dibromo-3-chloropropane	4
1,2,4-trichlorobenzene	20
hexachlorobuatdiene	4
napthalene	20
1,2,3-trichlorobenzene	4

Appendix 4C: Water quality data table

ID	well depth (m)	shale depth (m)	elevation (m)	geology	water type	Li (mg/L)	Be (mg/L)
1	76.20	738.05	67	Sanford	D	0.008	0.00002
2	68.58	208.84	55	Sanford	D	0.006	0.00003
3	67.06	937.00	82	Sanford	A	0.009	0.00000
4	83.82	1040.03	80	Sanford	A	0.005	0.00000
5	36.58	532.59	82	Sanford	A	0.005	0.00001
6	76.20	855.32	86	Sanford	B	0.014	0.00000
7	91.44	823.12	90	Sanford	A	0.011	0.00002
8	91.44	58.72	49	Cumnock	D	0.007	0.00003
9	106.68	442.71	86	Sanford	C	0.027	0.00000
10	64.01	922.18	62	Sanford	B	0.008	0.00002
11	42.67	68.39	55	Sanford	B	0.005	0.00002
12	60.96	1198.22	107	Sanford	A	0.007	0.00001
13		1199.20	190	unknown	A	0.006	0.00001
14	80.16	1211.61	88	Sanford	A	0.008	0.00000
15		11.04	100	unknown	D	0.008	0.00002
16	76.20	6.05	87	Cumnock	A	0.010	0.00000
17	39.62	0.00	75	Cumnock	A	0.006	0.00002
18	73.15	848.26	61	Sanford	C	0.017	0.00006
20	32.00	0.00	60	Cumnock	A	0.010	0.00001
21		1029.84	118	unknown	A	0.003	0.00002
22	30.48	1086.67	74	Sanford	A	0.003	0.00001
23	91.44	892.20	111	Sanford	A	0.010	0.00002
24	18.29	1177.79	33	Sanford	A	0.010	0.00001
26	38.10	1148.17	92	Sanford	A	0.007	0.00002
27	68.58	690.37	61	Sanford	B	0.008	0.00004
28	91.44	227.46	94	Sanford	D	0.009	0.00004
29	60.96	16.03	88	Cumnock	D	0.007	0.00002
30	99.06	724.01	114	Sanford	A	0.005	0.00004
31	53.34	1050.67	134	Sanford	B	0.007	0.00001
32		191.33	102	unknown	B	0.005	0.00001
33	11.73	185.58	79	Sanford	C	0.001	0.00005
34	36.58	261.25	94	Sanford	D	0.004	0.00003
35	53.34	1022.44	106	Sanford	A	0.005	0.00006
36	85.34	1027.77	130	Sanford	A	0.011	0.00002
37	60.96	861.95	120	Sanford	A	0.003	0.00003
38	48.77	1089.23	130	Sanford	A	0.016	0.00001
39	112.78	808.22	113	Sanford	D	0.011	0.00002
40	39.01	724.32	79	Sanford	D	0.006	0.00002
41	97.54	2.56	84	Cumnock	A	0.008	0.00001
42	49.68	582.81	90	other	A	0.004	0.00001
43	91.44	790.51	112	Sanford	D	0.012	0.00002
44	106.68	1107.12	133	Sanford	A	0.007	0.00001
45	97.54	938.84	131	Sanford	B	0.009	0.00002
46	45.72	1102.45	114	Sanford	A	0.009	0.00002
47		1099.94	115	unknown	A	0.008	0.00000
48	64.01	926.55	109	Sanford	A	0.008	0.00000
49	54.86	564.27	112	Sanford	D	0.006	0.00000
50	25.91	1114.26	122	Sanford	A	0.007	0.00000
51	106.68	6.21	78	other	D	0.014	0.00000
52	68.58	177.38	93	Sanford	A	0.007	0.00000
53	106.68	680.57	111	Sanford	A	0.009	0.00000

ID	B (mg/L)	Na (mg/L)	Mg (mg/L)	Al (mg/L)	Si (mg/L)	Cl (mg/L)	Ca (mg/L)	V (mg/L)
1	0.061	43.782	9.821	0.004	7.355	27.894	29.402	0.001
2	0.068	38.596	12.171	0.004	10.035	30.619	41.351	0.001
3	0.016	13.151	6.043	0.000	13.964	4.122	34.882	0.008
4	0.029	11.232	13.549	0.000	18.819	12.709	36.807	0.007
5	0.051	24.493	8.885	0.000	10.289	18.884	23.469	0.002
6	0.023	41.485	7.453	0.000	10.327	8.305	28.103	0.003
7	0.075	17.454	7.559	0.003	14.759	13.734	36.544	0.003
8	0.078	74.936	10.805	0.004	9.565	69.521	25.855	0.001
9	0.043	74.616	39.789	0.002	8.959	291.010	117.782	0.003
10	0.044	33.202	6.486	0.005	11.927	6.537	27.169	0.003
11	0.052	21.477	3.660	0.002	12.431	4.337	12.648	0.001
12	0.009	7.927	5.921	0.002	15.569	7.369	31.773	0.002
13	0.009	6.848	4.929	0.003	13.157	6.806	24.392	0.002
14	0.008	9.672	6.860	0.002	15.035	6.160	30.481	0.003
15	0.023	36.927	22.682	0.004	13.594	99.277	54.376	0.002
16	0.010	10.381	7.660	0.003	15.528	6.667	19.405	0.003
17	0.027	13.752	14.385	0.002	20.692	10.839	48.676	0.000
18	0.261	86.464	3.077	0.007	7.187	85.780	14.269	0.004
20	0.017	7.434	7.570	0.002	17.712	17.695	25.501	0.000
21	0.006	8.384	6.380	0.005	21.060	7.029	11.370	0.005
22	0.007	9.633	2.670	0.002	14.350	9.715	16.013	0.001
23	0.019	15.512	5.808	0.005	15.836	4.377	32.209	0.004
24	0.015	12.034	3.954	0.004	14.766	3.473	37.209	0.021
26	0.013	9.655	9.472	0.003	15.177	6.068	41.533	0.004
27	0.197	58.449	9.606	0.002	8.098	16.814	25.241	0.000
28	0.048	60.683	20.415	0.001	7.651	71.486	47.826	0.001
29	0.054	48.087	8.020	0.006	8.819	33.555	24.549	0.001
30	0.034	14.803	4.132	0.007	9.732	11.623	20.174	0.004
31	0.007	9.417	4.238	0.001	17.196	5.080	7.827	0.003
32	0.026	28.460	7.235	0.001	11.518	6.094	16.536	0.007
33	0.014	16.344	5.218	0.051	6.961	27.014	7.261	0.001
34	0.133	64.500	9.608	0.002	13.710	37.176	22.640	0.001
35	0.012	12.919	8.996	0.005	9.965	17.950	31.234	0.002
36	0.020	15.724	7.330	0.005	11.401	7.910	22.831	0.008
37	0.012	9.872	2.156	0.154	9.940	12.726	8.891	0.001
38	0.025	14.973	6.589	0.002	11.767	4.096	27.494	0.009
39	0.080	51.500	12.035	0.011	8.752	71.337	55.746	0.002
40	0.065	46.800	9.841	0.009	9.116	31.089	33.133	0.001
41	0.014	10.393	12.255	0.003	18.666	10.307	21.602	0.003
42	0.007	8.662	6.119	0.002	20.118	3.606	9.682	0.004
43	0.070	37.000	12.810	0.004	10.019	38.907	85.941	0.014
44	0.021	13.706	15.121	0.002	8.624	4.356	53.670	0.002
45	0.074	31.600	5.296	0.003	10.630	5.868	19.689	0.003
46	0.025	15.659	7.214	0.004	12.462	7.006	26.089	0.005
47	0.019	14.954	6.565	0.006	11.154	3.710	30.317	0.009
48	0.046	22.773	8.838	0.001	11.590	8.550	28.790	0.007
49	0.034	23.178	9.681	0.007	12.028	30.770	28.009	0.011
50	0.008	10.338	5.187	0.004	14.887	5.130	34.887	0.003
51	0.054	71.517	9.412	0.002	14.571	64.099	32.759	0.002
52	0.028	14.401	15.993	0.001	22.049	8.949	24.573	0.001
53	0.035	21.818	6.111	0.003	13.637	9.163	24.910	0.004

ID	Cr (mg/L)	Mn (mg/L)	Fe (mg/L)	Co (mg/L)	Ni (mg/L)	Cu (mg/L)	Zn (mg/L)	As (mg/L)
1	0.001	0.061	0.040	0.00028	0.001	0.002	0.004	0.002
2	0.001	0.124	0.039	0.00028	0.001	0.000	0.009	0.002
3	0.001	0.000	0.017	0.00000	0.000	0.001	0.002	0.002
4	0.001	0.000	0.015	0.00000	0.001	0.001	0.005	0.001
5	0.001	0.192	0.016	0.00014	0.001	0.001	0.009	0.003
6	0.000	0.000	0.024	0.00003	0.001	0.001	0.004	0.001
7	0.000	0.003	0.028	0.00016	0.001	0.003	0.002	0.002
8	0.002	0.057	0.028	0.00023	0.001	0.004	0.001	0.002
9	0.007	0.118	0.026	0.00059	0.004	0.003	0.006	0.001
10	0.001	0.000	0.024	0.00023	0.001	0.001	0.004	0.003
11	0.000	0.015	0.023	0.00012	0.000	0.001	0.003	0.006
12	0.000	0.000	0.016	0.00016	0.001	0.001	0.058	0.002
13	0.000	0.001	0.021	0.00018	0.001	0.001	0.008	0.002
14	0.000	0.000	0.015	0.00015	0.001	0.002	0.005	0.003
15	0.002	0.823	0.057	0.00051	0.002	0.000	0.003	0.002
16	0.001	0.002	0.027	0.00014	0.001	0.001	0.049	0.005
17	0.000	0.196	0.325	0.00026	0.002	0.000	0.021	0.000
18	0.003	0.001	0.018	0.00018	0.000	0.005	0.005	0.002
20	0.001	0.514	4.753	0.00087	0.001	0.000	0.003	0.001
21	0.003	0.000	0.006	0.00011	0.002	0.041	0.002	0.001
22	0.001	0.000	0.028	0.00011	0.001	0.003	0.002	0.001
23	0.000	0.002	0.025	0.00024	0.002	0.001	0.012	0.001
24	0.001	0.001	0.030	0.00022	0.002	0.007	0.020	0.005
26	0.002	0.001	0.021	0.00021	0.002	0.000	0.004	0.001
27	0.001	0.018	0.023	0.00020	0.000	0.000	0.039	0.002
28	0.002	0.205	0.078	0.00021	0.001	0.001	0.006	0.001
29	0.001	0.298	0.006	0.00018	0.001	0.000	0.004	0.006
30	0.000	0.004	0.011	0.00030	0.001	0.013	0.012	0.001
31	0.001	0.000	0.005	0.00010	0.000	0.009	0.074	0.002
32	0.000	0.017	0.049	0.00013	0.001	0.003	0.029	0.028
33	0.001	0.003	0.238	0.00016	0.001	0.008	0.560	0.001
34	0.001	0.134	0.026	0.00014	0.001	0.000	0.009	0.001
35	0.001	0.001	0.006	0.00019	0.003	0.003	0.015	0.001
36	0.000	0.003	0.003	0.00015	0.001	0.001	0.086	0.004
37	0.001	0.001	0.109	0.00016	0.001	0.010	0.011	0.001
38	0.000	0.000	0.003	0.00015	0.001	0.000	0.002	0.003
39	0.002	0.336	0.016	0.00028	0.004	0.000	0.002	0.002
40	0.001	0.060	0.028	0.00016	0.002	0.001	0.025	0.003
41	0.001	0.401	0.007	0.00016	0.001	0.005	0.004	0.003
42	0.004	0.000	0.003	0.00010	0.000	0.002	0.003	0.002
43	0.002	0.000	0.011	0.00053	0.002	0.007	0.013	0.002
44	0.000	0.003	0.013	0.00028	0.002	0.001	0.002	0.004
45	0.000	0.002	0.013	0.00010	0.001	0.002	0.035	0.003
46	0.000	0.001	0.000	0.00018	0.001	0.002	0.005	0.003
47	0.000	0.000	0.014	0.00000	0.000	0.015	0.008	0.003
48	0.001	0.000	0.014	0.00000	0.000	0.011	0.004	0.002
49	0.001	0.145	0.012	0.00001	0.001	0.012	0.006	0.001
50	0.000	0.000	0.016	0.00000	0.000	0.003	0.005	0.001
51	0.002	0.014	0.068	0.00000	0.000	0.007	0.041	0.020
52	0.000	0.041	0.027	0.00000	0.000	0.002	0.003	0.004
53	0.000	0.000	0.030	0.00000	0.000	0.008	0.019	0.003

ID	Se (mg/L)	Br (mg/L)	Rb (mg/L)	Sr (mg/L)	Mo (mg/L)	Ag (mg/L)	Cd (mg/L)	Sb (mg/L)
1	0.00130	0.14678	0.001	0.403	0.00258	0.00000	0.00000	0.00020
2	0.00037	0.15203	0.001	0.944	0.00197	0.00000	0.00000	0.00018
3	0.00000	0.00000	0.002	0.286	0.00268	0.00000	0.00000	0.00012
4	0.00000	0.03085	0.002	0.294	0.00022	0.00000	0.00000	0.00007
5	0.00038	0.06787	0.001	0.212	0.00043	0.00000	0.00000	0.00009
6	0.00000	0.00000	0.000	0.118	0.00282	0.00000	0.00000	0.00007
7	0.00000	0.00000	0.001	0.450	0.00125	0.00000	0.00000	0.00020
8	0.00000	0.33104	0.001	0.458	0.00035	0.00000	0.00000	0.00017
9	0.00017	0.78732	0.002	1.830	0.00036	0.00000	0.00000	0.00035
10	0.00000	0.00000	0.001	0.387	0.00249	0.00001	0.00000	0.00016
11	0.00000	0.00000	0.000	0.116	0.00104	0.00000	0.00000	0.00012
12	0.00000	0.00000	0.002	0.060	0.00000	0.00000	0.00000	0.00007
13	0.00000	0.00000	0.004	0.062	0.00000	0.00000	0.00000	0.00007
14	0.00000	0.02556	0.003	0.077	0.00000	0.00000	0.00000	0.00011
15	0.00102	0.52450	0.001	0.309	0.00008	0.00000	0.00000	0.00006
16	0.00000	0.02730	0.002	0.063	0.00000	0.00000	0.00000	0.00011
17	0.00000	0.00000	0.001	0.408	0.00008	0.00000	0.00000	0.00019
18	0.00000	0.18575	0.001	0.206	0.00395	0.00000	0.00000	0.00017
20	0.00000	0.00000	0.001	0.093	0.00003	0.00000	0.00000	0.00009
21	0.00000	0.00000	0.001	0.040	0.00000	0.00000	0.00000	0.00008
22	0.00000	0.00000	0.001	0.036	0.00000	0.00001	0.00000	0.00006
23	0.00080	0.00000	0.001	0.097	0.00135	0.00000	0.00000	0.00010
24	0.00006	0.00000	0.002	0.308	0.00248	0.00000	0.00000	0.00009
26	0.00000	0.00000	0.002	0.183	0.00003	0.00001	0.00000	0.00008
27	0.00000	0.06933	0.001	0.427	0.00131	0.00000	0.00000	0.00014
28	0.00125	0.35261	0.001	0.615	0.00219	0.00001	0.00002	0.00014
29	0.00000	0.14257	0.001	0.390	0.00070	0.00000	0.00000	0.00009
30	0.00000	0.03643	0.001	0.115	0.00017	0.00001	0.00000	0.00013
31	0.00000	0.01326	0.001	0.046	0.00000	0.00000	0.00000	0.00012
32	0.00000	0.01225	0.001	0.271	0.00023	0.00000	0.00002	0.00016
33	0.00011	0.00000	0.000	0.092	0.00000	0.00000	0.00024	0.00020
34	0.00000	0.17334	0.000	0.263	0.00043	0.00000	0.00000	0.00014
35	0.00006	0.03520	0.003	0.134	0.00029	0.00001	0.00002	0.00014
36	0.00071	0.00000	0.003	0.258	0.00010	0.00000	0.00001	0.00016
37	0.00053	0.02820	0.001	0.069	0.00000	0.00001	0.00001	0.00015
38	0.00000	0.02794	0.001	0.239	0.00000	0.00000	0.00000	0.00016
39	0.00000	0.40331	0.001	0.781	0.00008	0.00000	0.00000	0.00016
40	0.00079	0.15806	0.001	1.460	0.00105	0.00001	0.00000	0.00017
41	0.00043	0.03379	0.001	0.142	0.00000	0.00000	0.00002	0.00034
42	0.00000	0.00000	0.000	0.068	0.00000	0.00000	0.00000	0.00011
43	0.00000	0.18461	0.004	1.196	0.00278	0.00000	0.00000	0.00027
44	0.00000	0.01837	0.005	0.417	0.00000	0.00000	0.00000	0.00020
45	0.00018	0.00000	0.001	0.300	0.00532	0.00000	0.00000	0.00007
46	0.00073	0.03474	0.003	0.277	0.00031	0.00000	0.00000	0.00013
47	0.00013	0.03000	0.006	0.173	0.00376	0.00000	0.00000	0.00000
48	0.00055	0.05000	0.001	0.216	0.00485	0.00000	0.00000	0.00000
49	0.00059	0.18000	0.001	0.152	0.00367	0.00000	0.00001	0.00000
50	0.00000	0.03000	0.001	0.085	0.00387	0.00000	0.00000	0.00000
51	0.00061	0.84839	0.002	0.701	0.00154	0.00000	0.00000	0.00000
52	0.00000	0.00000	0.001	0.113	0.00522	0.00000	0.00000	0.00000
53	0.00026	0.00000	0.001	0.182	0.00424	0.00000	0.00001	0.00000

ID	Ba (mg/L)	Tl (mg/L)	Pb (mg/L)	Th (mg/L)	U (mg/L)	NO_3-N (mg/L)	SO_4 (mg/L)	$CaCO_3$ (mg/L)
1	0.175	0.00000	0.00001	0.00000	0.000	0.000	4.138	169.583
2	0.646	0.00000	0.00001	0.00000	0.001	0.007	4.271	150.178
3	0.220	0.00000	0.00000	0.00000	0.004	0.631	18.570	196.988
4	0.444	0.00000	0.00013	0.00000	0.004	0.396	4.795	197.203
5	0.323	0.00000	0.00009	0.00000	0.003	0.238	8.079	121.831
6	0.086	0.00000	0.00030	0.00000	0.002	0.352	7.251	123.190
7	0.161	0.00000	0.00024	0.00000	0.006	0.000	4.383	171.342
8	0.380	0.00000	0.00010	0.00000	0.003	0.014	14.946	171.177
9	0.685	0.00000	0.00000	0.00000	0.001	0.078	8.938	122.097
10	0.109	0.00000	0.00019	0.00000	0.002	0.415	5.793	122.399
11	0.058	0.00000	0.00141	0.00000	0.000	0.293	6.237	156.163
12	0.237	0.00000	0.00025	0.00000	0.001	1.527	2.236	156.011
13	0.304	0.00000	0.00030	0.00000	0.001	1.157	1.599	163.426
14	0.353	0.00000	0.00263	0.00000	0.001	1.157	2.496	163.599
15	0.186	0.00000	0.00028	0.00000	0.015	0.015	4.557	177.977
16	0.037	0.00000	0.00006	0.00000	0.001	0.165	4.319	178.686
17	0.206	0.00000	0.00016	0.00000	0.000	0.000	3.206	244.828
18	0.073	0.00000	0.00051	0.00000	0.002	0.062	13.024	244.439
20	0.019	0.00000	0.00001	0.00000	0.000	0.000	13.370	149.309
21	0.045	0.00000	0.00037	0.00000	0.000	0.500	1.205	70.471
22	0.079	0.00000	0.00017	0.00000	0.000	0.678	2.454	70.420
23	0.086	0.00000	0.00035	0.00000	0.002	0.167	16.219	115.350
24	0.074	0.00000	0.00093	0.00000	0.004	0.277	30.788	115.744
26	0.091	0.00000	0.00004	0.00000	0.001	0.345	90.729	90.054
27	0.083	0.00000	0.00013	0.00000	0.000	0.000	21.017	120.428
28	0.620	0.00001	0.00011	0.00000	0.001	0.000	5.278	120.598
29	0.144	0.00000	0.00012	0.00000	0.000	0.053	3.005	182.955
30	0.124	0.00000	0.00034	0.00000	0.001	13.109	7.294	183.242
31	0.120	0.00000	0.00045	0.00000	0.000	4.828	2.391	96.435
32	0.151	0.00000	0.00017	0.00000	0.010	0.005	4.154	97.166
33	0.055	0.00001	0.00553	0.00000	0.000	0.000	21.690	217.296
34	0.237	0.00000	0.00041	0.00000	0.001	0.000	8.536	216.427
35	0.215	0.00000	0.00008	0.00000	0.001	16.800	4.031	143.263
36	0.537	0.00000	0.00006	0.00000	0.005	3.359	4.667	143.386
37	0.146	0.00000	0.00030	0.00000	0.000	6.756	2.576	35.906
38	0.256	0.00000	0.00005	0.00000	0.006	0.019	5.382	35.837
39	0.471	0.00000	0.00056	0.00000	0.003	0.017	5.990	83.323
40	0.407	0.00000	0.00016	0.00000	0.001	0.154	7.659	83.090
41	0.034	0.00000	0.00010	0.00000	0.000	3.769	10.616	67.058
42	0.022	0.00000	0.00033	0.00000	0.000	0.051	1.526	66.832
43	0.334	0.00000	0.00000	0.00000	0.013	0.537	117.259	61.312
44	1.073	0.00000	0.00010	0.00000	0.004	15.673	7.498	54.340
45	0.292	0.00000	0.00008	0.00000	0.016	0.189	4.339	121.871
46	0.256	0.00000	0.00006	0.00000	0.005	10.661	3.961	121.837
47	0.574	0.00000	0.00003	0.00000	0.007	0.200	3.600	108.527
48	0.341	0.00000	0.00283	0.00000	0.004	0.210	3.350	108.727
49	0.372	0.00000	0.00018	0.00000	0.008	0.280	6.800	16.472
50	0.062	0.00000	0.00008	0.00000	0.002	0.310	1.350	15.303
51	0.410	0.00000	0.00002	0.00000	0.001	0.000	5.569	87.620
52	0.081	0.00000	0.00002	0.00000	0.000	0.000	0.710	87.960
53	0.098	0.00000	0.00020	0.00000	0.003	0.742	0.473	186.431

ID	HCO_3 (mg/L)	TDS (mg/L)	CH_4 (mg/L)	δ^{13}C-DIC ‰ VPDB	δ-H_2O ‰ V-SMOW	δ^{18}O-H_2O ‰ V-SLAP
1	195.109	211.191	0.06010	-17.051	-30.739	-5.313
2	240.523	245.967	0.00000	-18.380	-29.875	-5.404
3	149.505	150.942	0.00000	-16.649	-28.797	-4.683
4	208.994	182.219	0.00000	-19.233	-27.419	-4.181
5	149.184	157.428	0.03983	-14.100	-33.036	-5.504
6	190.480	186.401	0.00000	-17.330	-29.598	-5.226
7	199.541	177.900	0.00000	-18.518	-33.795	-5.592
8	217.625	303.502	0.23733	-20.000	-28.112	-4.935
9	298.536	681.113	0.00000	-17.404	-33.300	-5.674
10	183.316	169.814	0.00000	-19.100	-29.726	-5.554
11	85.968	90.892	0.00561	-19.346	-27.348	-5.418
12	141.006	125.906	0.00000	-15.645	-24.998	-5.123
13	110.435	99.905	0.00000	-16.138	-26.586	-5.325
14	147.067	128.993	0.00000	-17.200	-33.116	-5.438
15	223.442	328.154	0.01200	-19.485	-31.254	-5.745
16	118.129	106.571	0.00317	-19.853	-29.646	-5.342
17	264.645	220.941	0.48407	-16.500	-28.815	-4.705
18	174.905	288.770	0.00069	-18.866	-33.095	-5.627
20	101.540	121.417	0.01098	-17.249	-27.453	-4.718
21	81.696	74.939	0.00000	-18.244	-33.399	-5.770
22	70.568	75.778	0.00000	-11.700	-34.161	-5.589
23	148.704	147.253	0.00000	-15.959	-30.784	-5.299
24	132.562	152.998	0.00000	-18.085	-35.383	-5.576
26	107.134	210.481	0.00000	-16.508	-33.200	-5.397
27	226.625	242.669	0.00680	-19.200	-29.368	-5.161
28	295.269	351.337	0.05100	-18.700	-33.552	-5.708
29	207.989	219.715	0.05000	-22.200	-34.599	-6.796
30	94.336	117.509	0.00000	-10.100	-30.696	-6.277
31	60.853	63.658	0.00000	-15.400	-27.801	-5.451
32	158.394	140.380	0.00590	-19.200	-31.004	-5.940
33	28.430	91.549	0.00230	-16.300	-26.297	-4.961
34	251.732	266.245	0.02952	-21.300	-32.537	-6.479
35	88.768	135.595	0.00000	-12.000	-29.242	-5.954
36	146.712	133.967	0.00000	-16.100	-33.000	-6.436
37	43.424	64.352	0.00000	-8.400	-34.892	-5.873
38	165.929	140.125	0.00000	-16.800	-34.923	-6.301
39	282.285	336.128	0.01126	-17.000	-30.468	-5.800
40	242.813	249.272	0.05442	-19.200	-28.258	-5.285
41	151.214	143.212	0.00000	-19.900	-32.512	-5.334
42	88.024	72.846	0.00000	-21.200	-32.776	-5.945
43	259.852	421.163	0.00012	-17.700	-28.058	-5.344
44	262.689	239.178	0.00051	-18.400	-30.815	-5.860
45	180.368	155.662	0.00027	-18.700	-29.166	-5.639
46	151.082	144.931	0.00180	-17.800	-35.832	-6.460
47	168.156	141.946	0.00000	-17.900	-34.433	-6.195
48	185.071	163.462	0.00000	-19.000	-33.006	-6.198
49	142.274	168.764	0.03133	-18.500	-28.032	-4.974
50	156.142	133.826	0.03232	-17.200	-28.230	-4.641
51	236.907	300.990	0.01418			
52	179.649	152.768	0.00007			
53	142.279	133.115	0.00000			

ID	^{87}Sr/ (pCi/L)	^{226}Ra (pCi/L)	^{228}Ra	^{226}Ra/ ^{228}Ra
1	0.712	0.031	0.608	19.689
2	0.712	0.106	1.471	13.933
3	0.712			
4	0.712	0.025	0.420	16.594
5	0.712	0.018	0.284	15.523
6	0.712			
7	0.712			
8	0.711	0.044	0.813	18.492
9	0.712	0.175	4.567	26.041
10	0.712			
11	0.709			
12	0.713	0.026	0.577	22.466
13	0.713			
14	0.712	0.023	0.455	19.960
15	0.712			
16	0.712	0.005	0.079	15.425
17	0.709	0.017	0.367	21.317
18	0.713			
20	0.710	0.005	0.010	1.835
21	0.709	0.003	0.082	25.565
22	0.713			
23	0.712	0.005	0.000	
24	0.711			
26	0.711	0.012	0.098	7.888
27	0.712			
28	0.712			
29	0.712			
30	0.712	0.009	0.157	16.762
31	0.712	0.006	0.092	14.789
32	0.709			
33	0.709			
34				
35	0.713			
36	0.712			
37	0.712			
38	0.712			
39	0.713			
40	0.712			
41	0.712			
42	0.709			
43	0.712			
44	0.711			
45	0.712			
46	0.712			
47	0.712		0.348	
48	0.712			
49	0.712	0.039	0.465	11.923
50	0.712			
51	0.710	0.033	0.346	10.401
52	0.710			
53	0.712	0.009	0.152	17.236

5

Conclusions

5.1 Urban methane source identification using C isotopes and ethane

Phillips et al. (2013) identified numerous point sources of CH_4 on the streets of Boston, MA, likely from leaks in the natural gas distribution system. Subsequent work in other cities has found similar patterns of CH_4 emissions on streets (Jackson et al., 2014). I built upon these findings by comparing the δ^{13}C-CH_4 and [CH_4] / [C_2H_6] of 107 samples collected from CH_4 point sources on streets of Boston, MA, to the δ^{13}C-CH_4 and [CH_4] / [C_2H_6] for biological CH_4 sources in the urban environment (landfill, wetland, and wastewater treatment) and pipeline natural gas. Both the δ^{13}C-CH_4 and [CH_4] / [C_2H_6] signature of the street samples was indistinguishable from that of pipeline samples, but significantly different than that for all types of biogenic samples. My findings support those of Phillips et al. (2013) that leaks in the natural gas infrastructure are the primary source of CH_4 present on the streets of Boston. I also build on those results by including a larger set of samples for street leaks and for CH_4 point sources, as well as analysis of C_2H_6, which was not done by Phillips et al. (2013).

I provided additional confirmation that pipeline natural gas is the dominant source of the CH_4 in street samples. I have shown that the [CH_4] / [C_2H_6] of street samples are similar to that of a constructed time series of the [CH_4] / [C_2H_6] of the pipeline natural gas entering Boston based on publicly available data from pipeline transmission companies.

I investigated other possible sources for thermogenic CH_4 emissions by driving mobile [CH_4] surveys around compressed natural gas (CNG) bus depots, CNG filling stations, gasoline filling stations, an industrial propane tank, and a large liquified natural gas (LNG) import terminal. Based on these surveys, gasoline filling stations, CNG bus depots, and propane storage do not appear to be a significant source of CH_4 to the atmosphere. While I found no CH_4 emissions from the LNG import terminal, quantifying emissions from this facility more precisely will require further study. In contrast, areas near CNG filling stations had elevated [CH_4] during every survey, suggesting that these facilities may be large CH_4 sources locally. However, their cumulative significance to the regional CH_4 budget remains unclear, due to their small number.

5.2 Partitioning the biological and thermogenic contribution to the total methane flux in Boston, MA

There is increasing evidence that urban areas are large sources of CH_4 flux to the atmosphere (Mays et al., 2009; Wunch et al., 2009; Townsend-Small et al., 2012; Peischl et al., 2013). However, the details of urban methane budgets, particularly the relative strength of different CH_4 sources in urban areas, remain unclear. Building on the [CH_4] / [C_2H_6] and δ^{13}C-CH_4 signatures of urban CH_4 sources developed in the previous chapter, I used rooftop measurements of [CH_4], [C_2H_6], and δ^{13}C-CH_4 in Boston, MA, to determine that 88% of the CH_4 enhancement in the urban atmosphere between November 2012 and January 2013 was due to pipeline natural gas.

This result is based on a comparison of the measured [CH_4] and [C_2H_6] enhancement and the [CH_4] / [C_2H_6] signature of the pipeline natural gas composition time series developed in the previous chapter. The measured rooftop data are processed to include only the subset that best represents the well-mixed urban atmosphere. A bootstrapping approach suggests small uncertainty in the estimate of the contribution of pipeline natural gas to the total atmospheric [CH_4] enhancement (95% bootstrap confidence interval: 82–94%).

In addition to partitioning between sources of total CH_4 flux, these rooftop data provide insight into the source of individual CH_4 enhancements. I found that the [C_2H_6] / [CH_4] ratio was a useful tool for inferring the source of specific CH_4 peaks, and that δ^{13}C-CH_4 could provide further confirmation of source type (biogenic or thermogenic), although only for peaks with a large range of [CH_4] values. By comparing CH_4 source type to wind direction, I found that the majority of biological CH_4 enhancement in downtown Boston came from the direction of the only wastewater treatment plant in the region, $\sim$15 km distant from the sampling site.

Much work remains to establish a complete CH_4 budget for Boston, MA, which could inform research and emissions reductions in other locations. The CH_4 partitioning algorithm presented here will be combined with an overall CH_4 flux estimate for the Boston area to create a more detailed CH_4 budget for the region. Further study to refine this CH_4 budget could include bottom-up CH_4 estimates from urban sources, particularly the natural gas distribution system. As Brandt et al. (2014) have documented, uncertainty in CH_4 emissions factors can lead to considerable disagreement between bottom-up and top-down emissions estimates for all stages of the natural gas production chain, from resource extraction to end-use distribution. Studies of urban CH_4 emissions, including the work presented here, have demonstrated the importance of natural gas distribution to the urban CH_4 budget. However, emissions factors for this source do not yet exist. More detailed CH_4 accounting will require

emissions factors for the low-pressure natural gas distribution system, possibly based on mileage and material of natural gas mains.

Although uncertainty remains in the CH_4 budget in Boston, it would also be a useful comparison to study CH_4 emissions in other cities. Thus far, much of the work on urban CH_4 emissions has taken place in large cities in the United States (Jackson et al., 2014; Miller et al., 2013; McKain et al., 2012) and Europe (Nisbet, 2005; Kuc et al., 2003; Zinchenko et al., 2002; Lowry et al., 2001). The infrastructure in many of these cities is relatively old, which could lead to greater CH_4 flux than would be observed from more modern distribution systems. Studies of more recent developments, including lower-density suburban areas, are important in developing CH_4 emissions factors that are broadly applicable, particularly in the U.S. where population density is relatively low in many areas. Cities in developing countries are much less studied than those in the developed world, and could have different CH_4 budgets with potentially large overall CH_4 flux rates. The relative strength of the urban CH_4 sources in tropical areas with potentially more biological CH_4 production could be different than those observed in the temperate mid-latitude cities that have been most extensively studied previously.

5.3 Water quality in the Deep River Triassic Basin, NC

Background water quality data that can provide before-and-after comparisons has emerged as an important tool for better understanding the hydrogeologic and biogeochemical impacts associated with hydraulic fracturing for natural gas and oil (Down et al., 2013). In collaboration with others, I sampled 53 private drinking water wells and created a background water quality data set, including dissolved gases, volatile organic compounds (VOCs), major ions, and trace elements for the Deep River Triassic Basin in central NC, an area that could have hydraulic fracturing in the future. North Carolina is unique amongst areas that have hydraulic fracturing in that it

has no history of commercial oil and gas extraction that could influence pre-drilling water quality.

Only two samples contained dissolved CH_4 >0.1 mg/L, which is much lower [CH_4] than background measurements from areas above other shales, such as the Marcellus in PA (Jackson et al., 2013). Comparing the δ^{13}C-CH_4 of these shallow groundwater samples to that of two test gas wells drilled in the Deep River Basin, I conclude that the CH_4 in the water samples is produced biologically in situ and not derived from the undying Cumnock shale. The lack of [CH_4] enhancement in shallow groundwater and difference between δ^{13}C-CH_4 of groundwater and that of underlying CH_4 deposits suggests that widespread CH_4 migration from the shale to the surface is not occurring in the Deep River Basin, in contrast to the hydrologic connectivity observed in other areas (Warner et al., 2012).

Few groundwater samples exceeded federal or state water quality standards, and the standard that was exceeded by far the most often (16 of 53 samples) was the secondary standard for manganese. The samples contained very little existing VOC contamination (seven detections over five distinct samples), none of which exceeded a maximum contaminant level established by the U.S. Environmental Protection Agency. The absence of VOCs in groundwater is to be expected given the absence of a current or former industrial source in the region.

The background water quality presented here will be most useful paired with future follow-up measurements if the study area in the Deep River Triassic Basin is drilled for natural gas. In such case, water quality sampling similar to those described here performed at several time points (at a minimum, for example, during the drilling process and some length of time after) could help establish what changes accompany drilling, how widespread are those changes, and the temporal scales on which they occur. These data could be useful for policy makers focused on protecting the health of the public and the environment.

Appendix A

Shale Gas Extraction in North Carolina: Public Health Implications

This manuscript first appeared in the journal *Environmental Health Perspectives*, Down et al. (2013) as:

Down, A., Armes, M. and Jackson, R. B. (2013). Shale gas extraction in North Carolina: Research recommendations and public health implications. Environmental Health Perspectives, 121, A292–A293

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North Carolina has no history of large-scale commercial oil and gas extraction, and the states legislative framework for regulating drilling was, until recently, based on laws passed in the 1940s. However, areas of the state are likely to undergo horizontal drilling and hydraulic fracturing for natural gas and oil in the near future. North Carolina thus has a unique opportunity to produce a legislative framework that incorporates experiences from other states, includes state-of-the-art technologies and best practices, and protects the health of North Carolinas citizens and ecosystems.

Knowledge of the health risks associated with hydraulic fracturing is sparse. Some of the chemicals that can be used in the hydraulic fracturing process are toxic (Colborn et al., 2011; Bamberger and Oswald, 2012). However, the concentrations of these chemicals used at a given well site are not disclosed in most states, and evaluating the risk of exposure and associated health impacts is difficult. Residents living less than 1 kilometer from hydraulically fractured wells are potentially at greater risk for health effects from natural gas development in some cases, including exposure to trimethylbenzenes, xylenes, and aliphatic hydrocarbons in air (McKenzie et al., 2012). They can also, but do not always, have higher dissolved methane and other gases in their drinking water (Osborn et al., 2011a; Jackson et al., 2013; Warner et al., 2013a).

In October 2012, the Research Triangle Environmental Health Collaborative convened a summit of experts from the oil and gas industry, nonprofits, government organizations, and academia to consider the potential impacts of horizontal drilling and hydraulic fracturing in North Carolina. The summit included three working groups related to hydraulic fracturing: (1) exposure pathways, (2) health impacts, and (3) social impacts. The summit recommended actions and policies to safeguard the health of North Carolinas citizens and environment if hydraulic fracturing occurs in the state (Research Triangle Environmental Health Collaborative, 2012). The recommendations should also be useful for policy makers in other states.

Summit participants discussed numerous recommendations, with three categories having the broadest support. The first was the importance of collecting comprehensive background data of air quality, water quality, and human and ecosystem health before oil or gas drilling occurs. Such data provide a comparison to determine whether changes take place in the future, protecting both citizens and drilling companies from unfounded claims of damages. The quality and quantity of ground and surface water resources potentially affected by drilling should be studied, including analyses of major ions, trace metals, dissolved gases such as methane, radioactivity, and a range of organic compounds. Hydrocarbons from oil and gas wells should be characterized based on chemical and isotopic composition, which aids wastewater treatment and makes it easier to identify potential contamination if hydrocarbons are released into the environment. Ambient air monitoring of potential drilling areas is also important, as emissions from drilling sites may contain volatile organic compounds, particulates, and other contaminants. Ecosystem health, such as the identity and abundance of stream organisms, in the areas near drilling would ideally also be assessed.

A comprehensive Health Impact Assessment (HIA) was broadly supported as well, to monitor and avoid potential health problems in the future. An HIA should combine local, regional, and state level medical and demographic data. Tracking of any heath problems encountered in other states with hydraulic fracturing could provide early warning of heath problems that might occur in North Carolina and allow preventative action. Psychological and other stressors beyond direct chemical exposure should be considered, including sources such as increased road traffic and light and noise pollution. The HIA should also examine the potential economic costs associated with health impacts, including, for example, potential water remediation or increased rates of asthma.

The third broad recommendation was to create a Community Needs and Assets

Assessment (CNAA) to address potential social impacts. The CNAA should identify what jobs will be available to local workers, develop citizen stakeholder forums and reporting mechanisms, update transportation planning and safety training, and implement strong consumer protections. The working group on social impacts also recommended creating an ombudsman to facilitate communication between stakeholders and industry.

For all three recommendations discussed here, and for the many others in the report (Research Triangle Environmental Health Collaborative, 2012), it is important to clarify who is responsible for collecting such data and how to pay for it. One mechanism to ensure access for background data collection is to make gas well permits contingent on temporary site access for ambient air and water monitoring before, during, and after drilling and hydraulic fracturing. Policy makers might consider a bonding and remediation program to provide adequate cleanup, remediation, and maintenance funds. Performing comprehensive environmental or health remediation should be considered in assessing bonding fees. Finally, it is important to decide before drilling begins how increased costs of infrastructure maintenance and staff will be apportioned.

North Carolina has the opportunity to develop model programs and best management practices for shale gas drilling and hydraulic fracturing. Our recommendations complement the work of North Carolinas Mining and Energy Commission, and can help North Carolina and other states protect the publics health in areas undergoing unconventional oil and gas production.

Appendix B

Research Triangle Environmental Health Collaborative 2012 Annual Report

I was the primary author of the 2012 annual report by the Research Triangle Environmental Health Collaborative, *Shale Gas Extraction in North Carolina: Public Health Implications.* That report is reproduced here with the permission of he Research Triangle Environmental Health Collaborative.

B.1 Abstract

The North Carolina legislature recently legalized horizontal drilling and hydraulic fracturing. In hydraulic fracturing, millions of gallons of water, sand, and chemicals are pumped underground at high pressure to crack open rocks that hold oil and natural gas. Since becoming widely used over the past decade, the combination of horizontal drilling and hydraulic fracturing has greatly increased the amount of economically recoverable oil and natural gas. Hydraulic fracturing has also presented management challenges, both in terms of regulatory oversight and public perceptions.

Unlike some areas where hydraulic fracturing is becoming widespread, North Carolina has no history of oil and gas extraction on a commercial scale. Furthermore, the state's legislative framework for regulating drilling, authored in 1945, is based on outdated technologies. North Carolina is thus in a unique position among oil- and gas-producing states. Its new legislative framework can incorporate experiences from other states and include state-of-the-art technologies and best practices.

In October 2012, the Research Triangle Environmental Health Collaborative (EHC; www.environmentalhealthcollaborative.org/summit/summit-2012) convened a summit of experts to consider the potential impacts of hydraulic fracturing in North Carolina. Participants came from diverse stakeholder groups, including the oil and gas industry, nonprofits, government organizations, and academia. The EHC summit aimed to create a neutral space in which to share ideas and experiences to identify gaps in the current knowledge of, and preparations for, the potential impacts of hydraulic fracturing on public health in North Carolina. The summit recommended actions and potential policies to safeguard the health of North Carolinas citizens and environment if hydraulic fracturing occurs in the state. The recommendations, presented here, are directed towards state and local lawmakers in North Carolina to assist the work that North Carolina's Mining and Energy Commission

has begun.

The summit included three working groups related to hydraulic fracturing: (1) exposure pathways, (2) health impacts, and (3) social impacts. All three groups emphasized the importance of collecting comprehensive background data before oil or gas drilling occurs. Data collection should also continue after drilling takes place. Testing should include pre- and postdrilling testing for water quality and air emissions, as well as predrilling hydrogeology mapping, including information on faults, fractures, and groundwater flow. Measuring worker exposure during oil and gas extraction was also a priority, as was promoting a strong safety culture among oil and gas workers. Identifying and monitoring vulnerable species and ecosystems that could be impacted by drilling was also considered.

The working groups also highlighted some social impacts of horizontal drilling and hydraulic fracturing. The top recommendation was to create a Community Needs and Assets Assessment (CNAA), including identifying what jobs will be available to local workers, developing citizen stakeholder forums and reporting mechanisms, undergoing careful transportation planning and safety training, and implementing strong consumer protections. The group recommended creating an ombudsman to facilitate communication between stakeholders and industry.

The working group on potential health impacts made several suggestions, including developing a comprehensive Health Impact Assessment and participating in the Centers for Disease Control and Preventions National Environmental Public Health Tracking Network. A common thread running through the health recommendations was for the state to facilitate studies on medical and demographic data, as well as studies to generate exposure information for water- and air-based pathways. Finally, the group recommended that North Carolina mandate and fund an organization within the N.C. State Center for Health Statistics to establish baseline health data analysis of areas where hydraulic fracturing could occur.

B.2 Overview

B.2.1 Hydraulic Fracturing Process

Hydraulic fracturing is a method of extracting natural gas and oil (collectively called hydrocarbons) from deep within the Earth[1]. Within the past decade, the combination of horizontal drilling and hydraulic fracturing has greatly increased the amount of hydrocarbons that can be extracted at commercially viable prices. Although hydraulic fracturing technology has existed for decades, the combination of horizontal drilling and hydraulic fracturing is novel, and this combination that is referred to as "hydraulic fracturing"[2].

Hydraulic fracturing has proven particularly useful for extracting hydrocarbons from geological formations called shales. Natural gas drawn from these formations is referred to as "shale gas,"[3] and thus hydraulic fracturing also can be referred to as "shale gas extraction." Shales have relatively low permeability (Soeder, 1988), meaning that hydrocarbons (and other fluids) migrate slowly through shales. A gas well with a horizontal component has a longer path through the target formation than does a conventional gas well. The greater surface area of the shale exposed to the wellbore increases the amount of hydrocarbons that flow into the well and up to the surface. Horizontal drilling can extend two miles through shale formations.

Hydraulic fracturing is a process that further increases the amount of hydrocarbons that can be extracted from a well. The well is first perforated with small explosives, creating small fractures in the surrounding shale formation. This fracture

[1] The depth of hydrocarbon-bearing shale formations varies from less than 300 to more than 4000 meters (GAO, 2012b). Although hydrocarbons usually are extracted from several thousand feet below the Earths surface, water used for drinking and agriculture often is drawn from several hundred feet or less below the Earths surface.

[2] Hydraulic fracturing also is spelled "fracing" in industry publications. In this context, fracing usually refers specifically to the hydraulic fracturing operation, not necessarily in combination with horizontal drilling.

[3] This moniker is to distinguish methane from shales from that derived from so-called conventional sources, such as vertical gas wells that are not fracked.

network increases the surface area of the shale in contact with the well. High-pressure fracturing fluid is then pumped into the well, expanding the fracture network in the shale. The fluid contains particles, often sand, that prop open the rock fractures after the pressure of the fluid drops. Hydraulic fracturing fluid is composed primarily of water but also contains a number of chemical additives, such as corrosion inhibitors, biocides, and friction reducers, to optimize the performance of the gas well. The mix of chemicals used can vary depending on the properties of a specific well and the rock into which it is drilled. Drilling and hydraulically fracturing a single well can require several million gallons of fluid (Chesapeake Energy, 2010).

B.2.2 Impact on the Energy Sector

Natural gas supply in the United States has increased rapidly as a result of widespread hydraulic fracturing. Natural gas, as a fuel source to generate electricity, burns more cleanly than coal and emits less carbon dioxide per unit of energy produced. Moreover, burning coal releases mercury and coal ash to the atmosphere, thus contributing to pollution and particulate-related climate change, whereas burning natural gas does not.

The amount of electricity generated from natural gas in the United States nearly doubled between 1993 and 2011 (Office of Integrated Analysis and Forecasting, 2009) (figure B.1) and is projected to be nearly equal to that generated from coal by 2040. Although the use of natural gas for electricity generation has increased with the growth of shale gas extraction, the widespread availability and low cost of natural gas has lessened the economic incentive for some renewable energy sources, such as wind and solar (Harvey, 2012).

The United States has large shale gas and oil reserves[4]. Hence, natural gas is

[4] The most recent estimate by the U.S. Energy Information Administration for the United States shale gas reserves is 482 trillion cubic feet of natural gas. This is enough natural gas to supply the United States, at the current rate of consumption, for about 20 years (Urbina, 2012).

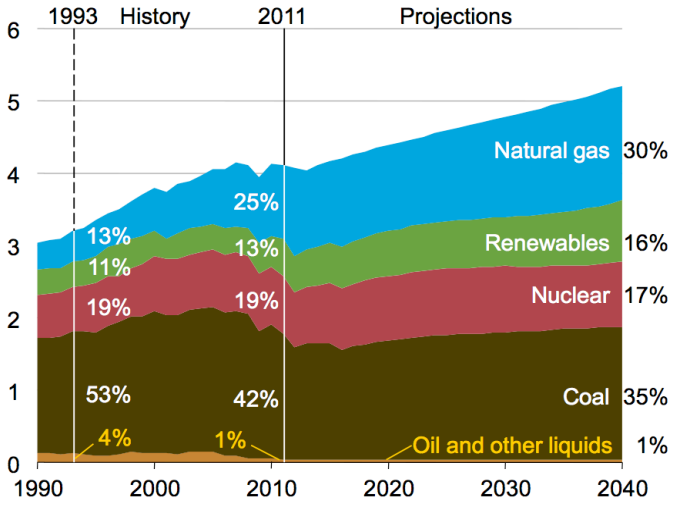

FIGURE B.1: U.S. electricity generation by energy source, in trillion killowatt hours. Electricity generation from natural gas has increased since hydraulic fracturing increased the natural gas supply in the mid 2000's (Office of Integrated Analysis and Forecasting, 2009).

a politically popular domestic energy source. Although hydraulic fracturing has proceeded quickly in the United States, there are other countries, such as China and India, that have large hydrocarbon reserves that have not yet been accessed. It is possible that hydraulic fracturing could lead to an era of increased natural gas use worldwide (Priddle, 2011).

B.2.3 Hydraulic Fracturing and North Carolina

North Carolina recently took steps to legalize horizontal drilling and hydraulic fracturing. Session Law 2011-276 required the N.C. Department of Environment and Natural Resources, the N.C. Department of Commerce, and the N.C. Department of Justice to evaluate the potential impacts of horizontal drilling and hydraulic fracturing on the state (North Carolina Department of Environment and Natural Resources, 2012). Following the release of that report, the state legislature, via Session Law 2012-143, mandated the creation of a board of commissioners to oversee the development of a modern oil and gas regulatory system in North Carolina.

The areas of North Carolina that may contain hydrocarbons are geologic basins that formed during the Triassic period, about 230 million years ago (Milici et al., 2012). There are two of these basins in North Carolina: (1) the Danville formation in northwestern North Carolina and southern Virginia and (2) the Deep River formation in central North Carolina. Of the two, the Deep River formation is the most likely to contain oil and gas[5].

The U.S. Geological Survey estimates the undiscovered natural gas resources in the Deep River Basin of North Carolina to be 1,660 billion cubic feet (1.66 trillion cubic feet) of gas and 83 million barrels of natural gas liquids (Milici et al., 2012). The Danville Basin is far smaller, containing and estimated 42 billion cubic feet of natural gas (Milici et al., 2012). For comparison, the estimated natural gas reserves in the Marcellus Shale, which underlies parts of Pennsylvania, New York, and West Virginia, are 84 trillion cubic feet (Urbina, 2011a).

Although significantly smaller than the Marcellus Shale in terms of surface area, hydraulic fracturing North Carolinas Deep River Triassic basin potentially could impact many people. Lee County, which contains most of the Sanford sub-basin, has a population density five times that of Bradford County, Pennsylvania, an area that overlies the Marcellus Shale and has been extensively drilled. The Deep River basin also extends into urban areas of Chatham, Wake, and Durham counties. Information about North Carolina's Triassic basins is currently limited, and it is difficult to predict whether future drilling in the state would extend into urban areas. Hydraulic fracturing in the state could affect residents farther from drilling sites through competition for surface water use, increased truck traffic on roads, disposal of hydraulic fracturing waste, and availability of housing and social services.

[5] The likelihood for a geologic formation to contain hydrocarbons and the form of those hydrocarbons depend on the amount and type of organic matter originally deposited in the formation, as well as the thermal history of the formation. Although existing data are limited, the hydrocarbon potential of the formations in North Carolina has been assessed by Reid and Milici (Reid and Milici, 2008).

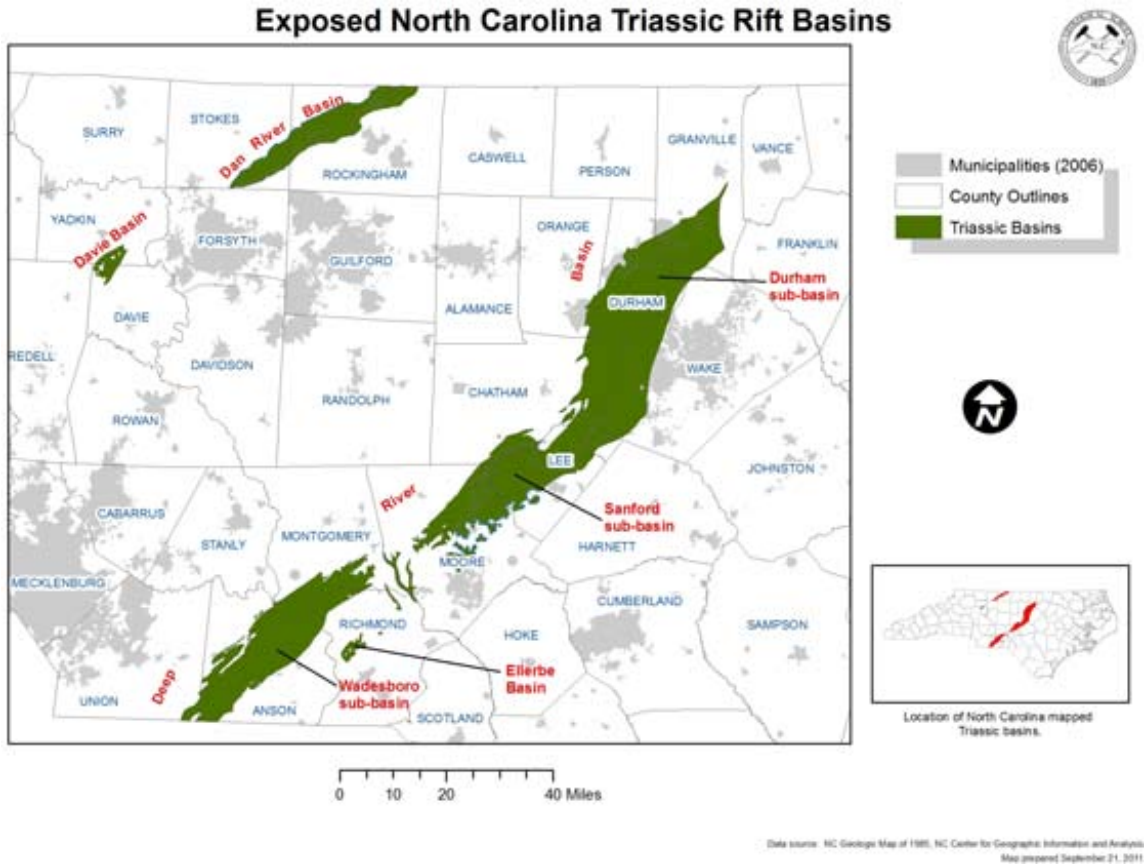

FIGURE B.2: Triassic rift basins in North Carolina (North Carolina Department of Environment and Natural Resources, 2012). The Sanford sub-basin in Lee County is the area most likely to be drilled for oil and gas when drilling begins. The Durham sub-basin extends northwards through urban areas of Wake, Durham, and Chatham Counties.

North Carolina has no history of commercial oil and gas development. Many other states in which hydraulic fracturing currently is occurring, such as Pennsylvania and Texas, have more than a century of experience with the oil and gas industry. North Carolina also currently does not have the staff in place to regulate or inspect drilling facilities.

The lack of a commercial oil and gas industry in North Carolina could be advantageous to the state. Because there has not been significant drilling for oil and gas, the state has an opportunity to collect background data before hydrocarbon

exploration and development occur. This data could provide a comparison to determine how the state is impacted by hydrocarbon development if it occurs in the future. North Carolina also has the opportunity to craft new legislation that reflects current technologies, incorporates the best scientific knowledge, and builds on the experiences of other states. The Environmental Health Collaborative summit was convened to gather this knowledge into recommendations for legislation to govern North Carolina's future with oil and gas.

B.2.4 Background Provided by the Institute of Medicine Meeting

The EHC summit built on the Institute of Medicine (IOM) of the National Academy of Sciences Workshop on the health impacts of shale gas, held April 30 and May 1, 2012. The IOM meeting was introduced and summarized at the opening of the EHC summit, and many of the themes from the IOM meeting were addressed.

Participants at the IOM meeting acknowledged that shale gas extraction is an emerging issue that will continue to be important for years. As such, it is imperative to understand the potential short- and long-term health impacts resulting from widespread shale gas drilling. The IOM meeting also focused on assessing the impacts from the complete lifecycle of shale gas extraction, from initial development of well pads to well decommissioning and final site reclamation. Like the EHC summit, the IOM meeting did not produce comments on the appropriate future course of hydraulic fracturing in the United States or elsewhere. Rather, the goal of the meeting was for participants to use the best available science to describe what should be done to better understand and mitigate potential health impacts from the proliferation of shale gas extraction.

Specific health concerns discussed at the IOM workshop, such as occupational hazards for oil and gas workers and community impacts from non-chemical stressors, are discussed below in further detail.

B.3 Summit Recommendations

B.3.1 Common Themes

The Environmental Health Collaborative (EHC) summit, held on October 2 and 3, 2012, included three separate working groups, each focusing on a class of issues relating to the potential for future drilling in North Carolina: (1) exposure pathways, (2) health impacts, and (3) social impacts. Each group compiled a list of the shortcomings in the current understanding of potential impacts of hydraulic fracturing. Groups also proposed recommendations for actions and legislation to address these gaps. Although the focuses of each group were different, there was overlap in the subjects considered and in the resulting recommendations. Themes and recommendations reached by multiple groups are described below. Recommendations by individual groups follow.

B.3.2 Baseline Data

The importance of collecting baseline data emerged as an important theme from every working group of the EHC summit and was also a priority identified at the IOM meeting. "Baseline data" refers to testing performed before oil and gas drilling takes place. Such data can provide a comparison to determine whether any changes have taken place as a result of activities associated with shale gas. This data then can be used to make changes in practice if necessary and may also protect both citizens and drilling companies from unfounded claims of damages.

There are a number of different types of background data that should be collected in North Carolina. Working groups at the EHC summit recommended the following statewide measurements:

- *Water quality.* The quality and quantity of ground and surface water resources potentially affected by drilling should be studied. Water sources should be as-

sessed, at least, for major ions, trace metals, dissolved gases (such as methane), radioactivity, and a range of organic compounds.

- *Hydrogeologic framework.* There should be a detailed mapping of the hydrogeologic framework, including rock types and fault structure, in gas drilling areas.

- *Hydrocarbon characterization.*Hydrocarbons should be characterized based on chemical and isotopic composition. Knowing the signature of hydrocarbons being extracted could improve wastewater treatment and make it easier to identify contamination if hydrocarbons are released into the environment. A starting point would be to extract fresh samples of the hydrocarbons from the oil and gas wells already present in North Carolina.

- *Air quality.* Airborne pollutants were identified by participants at the summit and the IOM meeting as a potential health hazard to oil and gas workers and state residents. Emissions from drilling sites could potentially contain heavy metals, volatile organic compounds, and other contaminants. Drilling areas should undergo ambient air monitoring.

- *Ecological data.* Ecosystem health in the areas potentially affected by hydraulic fracturing should be assessed.

- *Health data.* Population health statistics are essential in understanding what impact shale gas extraction has on the short- and long-term health of residents in affected areas.

Some of these data already exist in disparate sources and need to be compiled. Other data have not yet been collected and will require further field studies. Legislation is needed to clarify who is responsible for collecting such data and make adequate funding available to collect it.

One mechanism to ensure access for background data collection is to make gas well permits contingent on site access for ambient air and water monitoring before, during, and after the drilling and hydraulic fracturing processes. This requirement would not necessarily require drilling companies to pay for these measurements but would ensure that government and non-government researchers would be granted access to collect data where necessary.

B.3.3 Water and Wastewater Management Plan

Wastewater is produced as a byproduct of most oil and gas operations and increases dramatically when high-volume hydraulic fracturing occurs. Some hydraulic fracturing fluid, referred to as flowback fluid, returns to the surface soon after a well is hydraulically fractured. Liquid can continue to return to the surface long after the well has been fractured; such fluid is often called "produced water." Both flowback fluid and produced water can contain high concentrations of salts, organic compounds, and, in some cases, radioactivity[6]. These compounds are remnants of chemicals used in the original hydraulic fracturing fluid mixed with natural compounds resulting from interactions between fracturing fluid and rocks deep underground.

Flowback and produced waters are waste products that require careful management. Storing wastewater at the surface in containment ponds raises the possibility of unintentional leaks or discharges (Griswold, 2011). Wastes can be disposed of through deep injection (GAO, 2012a), in which waste fluids are pumped underground into porous geologic formations away from groundwater sources. However, the geology is not suitable for such injection wells in most of North Carolina. Moreover, deep injection wells for waste disposal have increased the likelihood of earthquakes in some areas (Seeber et al., 2004; Williams, 2011; Fountain, 2011). Treating waste

[6] Radioactivity is naturally occurring in some shales but not all. The Marcellus Shale in Pennsylvania, for example, is relatively more radioactive than other shales (Ayotte et al., 2011).

fluid in municipal wastewater treatment facilities, as has been done in other locations (Brown, 2011), is undesirable because municipal treatment facilities are not designed to deal with the types of compounds typically found in hydraulic fracturing waste, such as high salt levels and radioactivity. Wastes should be pre-treated at a centralized facility to reduce salt concentrations and radioactivity before being treated in municipal facilities. Land application is not a viable disposal option and has been shown to cause significant tree mortality (Adams, 2011). Many drilling companies are pursuing methods to reduce and recycle waste fluid, a positive development in locations such as the Marcellus shale.

Hydraulic fracturing can potentially impact local water availability. Drilling and hydraulic fracturing a well require large volumes of water: five million gallons or more might be used per well, depending on the specific geologic formation (Chesapeake Energy, 2010). The impact of these added water demands depend on the local water supply and the other potentially competing water users.

North Carolina should develop a comprehensive water and wastewater management plan. This plan should address how water is allocated between users and how priority is granted. It should have a strategy to handle droughts, including policies for dealing with periods of low water availability. Water allocation has consequences for residents who rely on a local water supply for residential or commercial use.

This management plan also should establish guidelines for background water testing. Monitoring should be in place before drilling occurs. Because of seasonal and annual variations in water quality and quantity, longer data collection periods make it easier to identify long-term changes if they occur.

B.3.4 Funding and Administration

The state should develop a bonding and remediation program to provide adequate cleanup, remediation, and maintenance funds. Drilling companies should pay into

a "premediation" fund financed by a permit fee to drill an oil or gas well. Current bonding laws usually pay only to cap gas wells when they are abandoned. However, performing more comprehensive environmental or health remediation should be considered in assessing bonding fees. It is important to decide, before drilling begins, how increased infrastructure maintenance costs will be apportioned. Increased truck traffic associated with shale gas can impact roads negatively, especially those in rural areas not designed to accommodate such traffic. The costs of maintenance and increased staff required to maintain roads should not be borne exclusively by the public.

More funding is needed to adequately address the potential environmental and social costs of hydraulic fracturing. Many of the recommendations in this document require funds that are not readily available and likely would not be covered by bonding measures. For example, collection of comprehensive environmental and health data can be expensive. Funding to collect this and other background data is required before, during, and after drilling occurs in the state. Monitoring and inspection should continue throughout the drilling process. Money also should be available for environmental and health remediation once drilling sites are retired, including remediation not associated with individual drilling sites.

Local, state, and regional agencies should coordinate the administration and oversight of hydraulic fracturing. Administration also should be coordinated in priorities, as well as actions, and duplication of effort between governing bodies should be minimized.

B.3.5 Best Management Practices

North Carolina should work with industry to promote a list of best management practices (BMPs) for drilling and hydraulic fracturing. This list should build on those developed in other states but be specific to North Carolina. These BMPs should fo-

cus on: preventing contaminants from entering the environment; containing contaminants if they do accidentally enter the environment; and monitoring for contaminants to quickly detect releases if they occur, stop them, and begin remediation.

Regulations are useful only to the extent to which companies comply. Effective regulations require enforcement if violations occur. Regulations must also keep pace with the rapid technological developments in the shale gas industry.

B.4 Working Group 1: Exposure Pathways

B.4.1 Overall Themes

The goal of analyzing potential exposure pathways is to reduce the incidence of exposure rather than mitigate exposures after they occur. Background information is essential to evaluate what chemicals are present and what can be considered a baseline state of human and environmental health. Understanding the links between chemical exposures and public health remains one of the greatest gaps in evaluating the potential impacts from shale gas.

B.4.2 Hydrogeologic Framework

Underground faults and fractures can serve as pathways for gas and fluid migration. It is unknown to what extent natural fault networks can facilitate migration of dissolved gases or hydraulic fracturing fluids from shale gas drilling. Nevertheless, understanding the geology and hydrology of the Deep River basin, particularly the Sanford sub-basin, is essential to evaluating the risks posed by hydraulic fracturing.

In addition to local fault structure, it is important to understand ground and surface water flows. The connectivity of groundwater sources can help assess both water availability for shale gas and spread of contamination should it occur. Surface water flows must be quantified to create a hydrologic budget that includes the water demands of shale gas. Understanding the local watershed also should include the

potential for dam ruptures or breaches of hydraulic fracturing fluid ponds.

4.2 Recommendations:

- *Generate a comprehensive state geologic map.* This map should include the local fault structure, as well as historical drilling and mining activities.

- *Establish drilling setback distances from geologic formations such as faults, fractures, and dikes.*

- *Generate publicly available data as part of the gas drilling and permitting process.* Drillers should collect and publicly release geologic information collected when drilling, including the amount of liquid condensate present in extracted gas.

- *Regulate well casing and cementing designs.* The well casing and cement are the key barriers between contaminants and the environment. As such, they should be strongly safeguarded. Casing depth standards should be established and enforced. Cement bond logs generated during well construction should be required to ensure that casing is adequately set. Well site design should be regulated to minimize exposures and contain contaminants if accidental releases occur. All drilling sites and pipelines should include automatic shutoff valves.

- *Require setback distances between hydraulic fracturing well sites and sensitive areas,* including private homes and water wells, surface water bodies, and sensitive ecological areas. Children can be especially sensitive to environmental contaminants, and special consideration should be given to establishing setbacks from schools, daycares, and other facilities with large numbers of young children.

- *Determine the prevalence of natural methane in shallow aquifers in the Deep*

River basin. Establishing a baseline for methane concentration in water resources used for drinking will be essential for evaluating whether dissolved gas contamination occurs in the future, should drilling occur.

- *Evaluate the radiological potential of North Carolina's geology.*

B.4.3 Hydraulic Fracturing Fluid and Wastes

The hydraulic fracturing process can involve numerous chemicals that are potentially toxic (Waxman et al., 2011). The composition of the hydraulic fracturing fluid used at a given site depends on the local geology and the drilling company involved. Regulations requiring the disclosure of hydraulic fracturing fluid contents vary by state (Deutch et al., 2011), particularly the extent to which chemicals can be excluded based on trade-secret exemptions. Information about chemicals used in the fracking fluid for many wells can be found at the industry's voluntary chemical disclosure registry, FracFocus (http://fracfocus.org/).

Assessing and minimizing the risk of exposure requires better knowledge of the composition of hydraulic fracturing fluid and waste waters. Environmental risk also depends on the volatility and mobility of compounds in the environment.

4.3 Recommendations:

- *Store all used fracturing fluids (flowback and produced water) and waste in closed tanks at the well site, not open pits, to minimize exposure risk and surface spills.*

- *Require inspections of well site contamination-prevention equipment,* including leak detection equipment, groundwater monitoring wells, and berm integrity.

- *Limit specific chemicals where capacity to track or assess health risk is not yet available.*

- *Develop a wastewater disposal plan.*

- *Require drilling companies to disclose hydraulic fracturing fluid composition.*

B.4.4 Water Quality

The surface water monitoring systems currently in place often are not designed to detect chemicals related to hydraulic fracturing. Groundwater monitoring data are also lacking in many locations. For example, there is little information on groundwater quality in the Deep River Triassic Basin at shallow depths, and to our knowledge none exist for depths greater than 1,000 feet. Heavy metals, salts, and other dissolved compounds in groundwater potentially could mix with chemicals in hydraulic fracturing fluid. Evaluating waste disposal options and potential hazards posed by flowback fluid requires knowledge of the composition of deep groundwater.

The number and quality of shallow groundwater wells in the Sanford sub-basin should also be studied. Many of these wells are used for drinking water or agriculture. Water wells that are poorly constructed could be at increased risk of damage from nearby drilling operations.

4.4 Recommendations:

- *Establish standards for baseline water testing.* These standards should prioritize analyses, as some homeowners may not be able to afford a complete suite. These standards and recommendations should be made easily available to homeowners. Potential sources for standards and expertise include the Division of Water Quality within the N.C. Department of Natural Resources and the N.C. branch of the U.S. Geological Survey.

- *Increase capacity for testing through interagency and intersector collaborations.* Standard protocols should be established so that measurements are comparable between sites and of known quality.

- *Reach out to industries that have experience in testing for organic compounds.* These industries also have experience in minimizing exposures. Examples include pesticide companies, confined animal feeding operations, and pharmaceutical companies.

- *Do not permit water withdrawals from streams whose flow is not gauged by the U.S. Geological Survey.*

- *Quantify the proportion of water withdrawal capacity that can be allocated to drillers.* Alternative water sources, such as reclaimed gray water and wastewater, also should be considered.

- *Monitor for surface water discharges around shale gas drilling and processing sites.*

- *Have drillers submit a water resources management plan as part of the permitting process.*

B.4.5 Air Emissions

Hydrocarbon drilling, processing, storage, and transmission can result in atmospheric emissions of volatile organic compounds (VOCs), including methane. Methane is a powerful greenhouse gas[7], and leaks of methane gas to the atmosphere as a result of hydraulic fracturing, gas transmission, or storage negatively impact the global climate. There currently is much debate over the approximate percentage of methane that is lost in the gas drilling and transmission processes (Jiang et al., 2011). Drilling often involves the use of heavy machinery, much of which is powered by diesel engines (Alvarez et al., 2012) which emit air pollutants. Each drilling operation involves

[7] Methane is 21 times more powerful than carbon dioxide as a greenhouse warming agent on a per-molecule basis (Pachauri and et. al., 2007).

many truck trips to transport water and materials to the drilling site, negatively impacting local air quality.

The quantity and type of emissions that occur during well completion[8] can vary and are not well quantified. Potential compounds of concern include, for example, hydrogen sulfide, volatile organic compounds, and other organic compounds such as benzene, toluene, ethylbenzene, and xylene. It is not known to what extent these compounds can volatilize from hydraulic fracturing fluid impoundment ponds.

Coal extracted from the Sanford sub-basin is high in sulfur (Reinemund, 1955), and it is unknown whether drilling could introduce sulfur compounds into the atmosphere. North Carolina soils also contain radon, and thus hydraulic fracturing potentially could create new pathways for radon to enter the atmosphere.

4.5 Recommendations:

- *Develop an air monitoring network.* This network should be based on the drilling processes in use and should integrate information from future changes in technology.
- *Establish standards for air sampling and incorporate them into industry best practices.*
- *Use air quality models to estimate regional impacts from distributed pollutant point sources.*

B.4.6 Employee Exposures

Oil and gas workers face numerous hazards at the job site. Absorption of compounds through the skin is a major exposure pathway for oil and gas workers. Compounds present on clothing, such as lead, also can be hazardous to family members when

[8] "Well completion" is the process which occurs after drilling in which equipment is put in place to gather the hydrocarbons coming out of the well bore.

workers return home. Prolonged exposure to respirable silica, used as a proppant in hydraulic fracturing fluids, can cause silicosis. Workers can be exposed when silica is being offloaded from trucks or moved on conveyers. Traffic and site dust are also contributors to silica exposure.

Hydrogen sulfide gas is another threat to oil and gas workers. This gas is toxic at low levels and can be fatal in high concentrations. Hydrogen sulfide co-occurs with hydrocarbons in some geologic formations, and it is released when so-called "sour gas" is brought to the surface. Bacteria in hydraulic fracturing fluids also can produce hydrogen sulfide, and reusing fluids can increase hydrogen sulfide concentrations in the fluids.

4.6 Recommendations:

- *There should be a site specific safety and health management program developed and implemented on every shale gas extraction site to address hazards*, such as but not limited to: occupational exposure to noise; confined space hazards; walking and working surfaces; flammable gases; radioactive materials; and exposure to hazardous chemicals.

- *Sand-handling equipment designed with engineering controls that prevent the generation of airborne dust or collect dust should be used.* Retrofit engineering controls and dust suppression and collection measures should be used on existing equipment.

- *Worker access to areas where respirable dust may be generated should be limited to only those workers wearing appropriate respiratory protection who are properly trained and medically cleared to do so.* When respirators are used on a shale gas extraction site, a comprehensive respiratory protection program should be developed and implemented[9].

[9] The program should be in compliance with 29 CFR 1920.134, and should apply even if employee

- *Silica sand should be replaced by a product that does not contain quartz.* Silica sand should be prohibited as an abrasive blasting agent.

- *Work site maintenance is a priority.* Because of the complexity of shale gas equipment and the pace at which the technology is changing, unspecialized workers no longer can perform onsite repairs.

- *Specific safety training is needed.* Rapid technological changes have led to numerous smaller companies providing well site services, some with little safety experience.

- *All injuries should be reported.* Current reporting of nonfatal injuries is incomplete.

- *There should be a competent person or other technically qualified person on site at all times who is responsible for ensuring that worker safety and health policies, practices, and procedures are implemented.*

- *Legislation and best practices should incorporate the best and most current information on shale gas worker safety and injury prevention.* Sources of information include the Occupational Safety and Health Administration[10] and The Centers for Disease Control and Prevention[11].

B.4.7 Ecosystem Exposures

Shale gas drilling can impact other species and ecological communities. Pet and livestock illness and mortality have been reported near drilling sites in Pennsylvania, Texas, and elsewhere (Bamberger and Oswald, 2012). Drilling can also impact natural ecosystems through chemical exposures and land use changes.

exposure is below the permissible exposure limit (PEL).

[10] www.osha.gov/dts/hazardalerts/hydraulic_frac_hazard_alert.html

[11] www.cdc.gov/niosh/programs/oilgas/default.html

It is important to determine what stressors are most likely to affect ecosystem health, which can help identify which components of an ecosystem are most at risk. Sentinel species, sensitive indicators of ecosystem health, include mussels, amphibians, and benthic macroinvertebrates. Other important species to consider are pollinators and recreational game and fish. Direct chemical exposure is not the only pathway by which natural gas extraction may affect wildlife. For example, in northern New Mexico, noise from natural gas compressor stations has altered bird species abundance toward those better able to communicate in a high-noise environment (Francis et al., 2009). Analyses should include direct and indirect exposures[12], as well as acute and cumulative long-term effects.

The roads, pipelines, well pads, and other infrastructure associated with shale gas extraction can fragment forests and streams (Morton et al., 2004). Expansion of sand mines in eastern North Carolina to provide silica for hydraulic fracturing fluids could create further habitat changes.

4.7 Recommendations:

- *Identify which species are most sensitive to chemical exposure.* The N.C. Division of Water Qualitys macroinvertebrate monitoring and the N.C. Wildlife Resources Commissions mussel monitoring could be expanded to help quantify these potential indicator species. Toxicity assessments should be conducted to establish thresholds of concern.

- *Identify which species are most sensitive to habitat loss.* Species distribution within the Triassic Basin is also important.

- *Identify areas that require special protections via setbacks and buffers.* These

[12] Indirect chemical exposures include contact with compounds that persist in the environment and are transported from the original emissions source. Examples could include drinking water contaminated by gas migrating from a hydraulic fracturing well or breathing air that contains particulates or organic compounds emitted from a drilling site.

areas could include conservation lands and wildlife corridors and areas important to resource-based industries such as forestry, agriculture, and fishing. The N.C. Wildlife Resource Commissions Green Growth Toolbox and the N.C. Department of Environment and Natural Resources Conservation Planning Tool could help identify areas that would be most sensitive to land use changes.

- *Monitor ecosystem health.* Baseline ecosystem health information should include pollutant levels in plant and animal tissues and evidence for adverse affects from chemical exposure. The distribution and density of populations, and their organismal pollutant levels, should be remeasured regularly. These measurements should inform future recommendations to further minimize exposure and health effects.

- *Establish numeric quality standards.* These standards should establish acceptable environmental levels of chemicals found in hydraulic fracturing fluids.

B.5 Working Group 2: Social Impacts

B.5.1 Community Needs and Assets Assessment

The primary recommendation to emerge from Working Group 2 was to *create a Community Needs and Assets Assessment* (CNAA). This document should be created in partnership between a community and local drilling companies before drilling takes place. Such documents are considered an industry best practice. The CNAA should identify methods that the industry can use to communicate the contents of the CNAA to the public. The recommendations presented below are intended to raise awareness of what a CNAA can and should include.

B.5.2 Economy

Distribution of Costs and Benefits

Much of the gas drilling currently occurring in the United States takes place on privately held property[13]. Because terms of leases are negotiated individually, and because not all property is equally suitable for shale gas extraction, income from shale gas is not distributed equally within a community. Inequality, actual or perceived, can lead to tension among residents.

Potential gas-producing areas in North Carolina are fairly rural, and the income from shale gas can be a large boost to the local economy. However, there is potential for shale gas to affect vulnerable populations more acutely than others. Residents in an economically depressed area may be more willing to accept oil and gas leases with unfavorable terms than those who have other income sources.

5.2.1 Recommendations:

- *Fully identify costs and benefits associated with shale gas.* Where a cost-benefit analysis is not possible, case studies drawn from the experiences of other areas can provide insight.

- *Maximize revenue available from industry.* Revenue can be generated through bonding fees on well permits and taxes assessed.

- *Identify what jobs will be available for local workers and how the shift in available workers could affect the local economy.* Unemployment in shale gas areas tends to be low. However, as a result, it can be difficult for some industries to recruit entry-level or unskilled workers (Shactman, 2011).

[13] Even in areas held by the Bureau of Land Management, mineral rights may be held separately from surface rights. For example, 90% of the mineral rights to the Allegheny National Forest in Pennsylvania are held privately (Andrews et al., 2009).

Boom and Bust Dynamic

The sudden influx of economic activity based around a single resource is vulnerable to boom and bust cycles. When resources are exhausted or economic conditions change, jobs can disappear quickly. Natural gas prices are historically volatile (Flavin and Kitasei, 2010), and swings in price could affect production, especially in a smaller resource area like North Carolina. Concerns over an end to shale gas booms in other areas have already been expressed (Urbina, 2011b).

5.2.2 Recommendations:

- *Build capacity to sustain economic activity.* Lawmakers and area planners should consider cultivating other industries that are less vulnerable to boom and bust cycles to maintain economic activity.

- *Identify where the industry will be operating and for how long.* Communities should prepare for times when industry is no longer present. Planners may have to look ahead decades to prepare for this eventuality.

B.5.3 Community Identity

Loss of Control over Community Identity

The economic and industrial activity accompanying shale gas could be a rapid and drastic transition for the Sanford sub-basin. This transition can be jarring for residents and can impact their quality of life. Examples of negative experiences resulting from this transition include

- increased truck traffic, resulting in road damage and higher levels of potentially harmful vehicle exhaust;

- disturbances and reduced access to private or public lands. For example, hunters in Pennsylvania have lost access to popular hunting areas on public

land because of nearby shale gas extraction (Seelye, 2011).

Shale gas can be a polarizing issue. As mentioned above, the land leasing system for shale gas can lead to real or perceived economic disparities among members of a community. The perception of a threat to ones health or environment, based on facts or emotions, can powerfully sway opinion. As a result of these deep divisions, relations within a community can become contentious.

5.3.1 Recommendations:

- *Communities should maintain control over local quality of life issues*, including local authority over zoning regulations.
- *Develop and promote mediation resources.*
- *Increase support to services that deal with mental health and psychosocial impacts.*

Quality of Life and Environmental Health

Shale gas activities can create odors, light pollution, noise, and dust. These and other environmental health impacts are especially important to consider near schools.

5.3.2 Recommendations:

- *Identify best practices and regulations to mitigate these impacts.*
- *Develop citizen reporting mechanisms.* These can include phone hotlines or online contact mechanisms, as well as publicly available maps of reported and confirmed violations.

B.5.4 Community Engagement

Effectively integrating shale gas into a community requires ongoing communication between drilling companies and that community.

5.4 Recommendations:

- *Identify who in the community is affected by shale gas development and who has the jurisdiction to take action.*
- *Create stakeholder forums.* These forums should aim to create two-way dialogs between public policy leaders and affected populations. Efforts should be made to include vulnerable populations in these forums.
- *Offer workshops for government officials.* Local officials should be briefed on what to expect when shale gas enters their community. These workshops would provide an avenue for community leaders to learn from and build on experiences in other areas.
- *Create educational mechanisms for potentially impacted communities.* Topics to discuss with residents include the following: how long the oil and gas industry could be present in the community, potential impacts from shale gas extraction, liability and consumer protection mechanisms, and air and water quality test results and how to obtain them.
- *The state should take the lead in community engagement, while maintaining contact with local officials and industry.*
- *Outreach events should be convened by a credible neutral party and include all stakeholders.*

B.5.5 Infrastructure

Roads and Vehicle Safety

Hydraulic fracturing of a single well site can require a thousand truck trips to and from the well site. Many roads, especially in rural areas, are not designed to handle

this large amount of truck traffic. Roads and bridges can rapidly degrade when engineered capacity is exceeded. Increased truck traffic also can be dangerous for drivers not used to driving in heavy truck traffic.

5.5.1 Recommendations:

- *Transportation planning agencies should plan ahead for increased traffic and capacity.*
- *New road permitting should be implemented in conjunction with oil and gas well permitting.* Roads necessary to provide supplies to shale gas sites should be included as part of the well site permit. These roads should be adequately engineered during the permitting process to withstand expected truck traffic.
- *Map transportation routes to and from sites.* Identify potential water sources, which could become heavy traffic areas. Understanding truck traffic patterns can help identify roads that are likely to need increased maintenance.
- *Coordinate school bus and trucking routes to separate them.*
- *Implement traffic pattern changes where necessary to protect vulnerable roads.*
- *Add signage to warn drivers of additional hazards.*
- *Widen roads and add pullouts for trucks.* Long trucks may need road modifications to navigate turns.
- *Ensure that industry pays incremental costs of road construction and safety measures.*
- *Trucks should be bonded, signed, and travel only on approved roads.*

Job Opportunities

Shale gas development can create jobs. The oil and gas industry requires many workers, but these workers are not always hired locally because of the need for specific worker training or lack of interest amongst local workers. Many other industries that support shale gas, however, such as trucking, restaurants, gas stations, and hotels, can see large upswings in business.

5.5.2 Recommendations:

- *Create educational programs to train local workers for available oil and gas jobs.*

Physical Infrastructure

The influx of people associated with shale gas can put increased strain on physical infrastructure, such as municipal water and sewer capacity and facilities.

5.5.3 Recommendations:

- *Ensure the infrastructure needs of the local community are met.*

Emergency Services

Shale gas extraction can be hazardous to workers. Emergency responders will be called on to deal with situations relating to gas extraction. The large influx of people associated with shale gas also will entail more emergency incidents simply because of the increase in population.

5.5.4 Recommendations:

- *Shale gas extraction operators should provide the following information to the county and municipality with jurisdiction and to emergency response agencies:* the nature and type of operations to occur at the facility; the properties of the hazardous materials managed at the facility; a copy of the contingency plan for the facility.

- *Shale gas extraction operators should maintain an up to date record of the quantity, type, location, and hazards of the chemicals used, produced and stored at the facility.* This information should be stored offsite, and should be made available to the Department of Environment Health and Natural Resources, any municipality with jurisdiction over the site of the facility, and to emergency response agencies that have a role under the contingency plan for the facility.

- *State and local governments should coordinate to map potential hazard areas.* These include well sites and gas transmission pipelines. These maps should be publicly accessible and provided to emergency response system dispatchers and responders.

- *Drilling companies should help provide training to local emergency medical services personnel where needed.* This should include additional training in areas such as hazardous materials and confined space rescue.

- *Fund staff needed to handle increased emergency services capacity.*

Social Services

Rapid population growth can cause strain on many social services. Shale gas can heighten needs for particular social services, such as

- attorneys with oil and gas experience;

- affordable housing supply, especially for transient or temporary residents (Prices for small housing and hotel rates have shot up in many areas of shale gas extraction, as workers without family in the area struggle to find housing (Galbraith, 2012));

- schools, which can see an influx of transient students that are children of oil and gas workers;

- law enforcement, courts, and correctional facilities.

5.5.5 Recommendations:

- *Community planners should expand local infrastructure in advance where possible.*

B.5.6 Landowner and Consumer Protection

Most homeowners in North Carolina have no prior experience with oil and gas development activities and may not be able to fully assess financial and environmental risks associated with shale gas leases. Moreover, there are few lawyers in North Carolina that have experience with the oil and gas industry to provide adequate legal guidance.

5.6 Recommendations:

- *Clarify liabilities of industry and landowner.*
- *Establish insurance mechanisms for property owners.*
- *Fund state laboratories to provide low-cost baseline water and air testing.* Tests that are inexpensive or free provide necessary protections to low-income communities. Provide education about mineral leases.
- *Create an ombudsman role to facilitate communication among homeowners, industry, and legal representatives.*
- *Invest in databases to compile water testing results and site history.* These data sources should be accessible to the public.
- *North Carolina needs to study the issues of compulsory forced pooling more closely*, in which homeowners can be required to engage in a gas lease if the

owners of many surrounding properties already have done so, subject to conditions.

B.6 Working Group 3: Health Impacts

B.6.1 Incomplete Information

Some of the data that are essential for evaluating the potential health risks associated with shale gas are not publicly accessible. For example, state laws vary in the extent to which the chemicals in hydraulic fracturing fluids are disclosed. Animal toxicity studies are typically performed with a single chemical, whereas fracturing fluid can contain many chemicals of varying concentrations.. Without more complete knowledge of the chemicals involved, their concentrations in the fluid, and their toxicity, it is difficult to assess their potential impact on human or animal health.

Other essential data have yet to be collected. Limited epidemiological data exist for populations potentially affected in North Carolina. These datasets are not sufficiently complete to serve as an adequate baseline for assessing future health changes at a population level.

6.1 Recommendations:

- *Leverage existing baseline health data in North Carolina and other states.*
- *Where data are not available, leverage knowledge of known chemicals and their toxicological effects.* Health care providers need to learn to identify possible symptoms of exposure to air- or water-borne contaminants from shale gas operations
- *Improve medical record keeping.* Move to electronic record keeping as much as possible.

- *North Carolina should become part of the Centers for Disease Control and Preventions National Environmental Public Health Tracking Network.*

B.6.2 Health Impact Assessment

Overview

North Carolina should conduct a comprehensive Health Impact Assessment (HIA)[14]. This assessment should gather available health data about communities in the Sanford sub-basin potentially affected by shale gas. The end product of this process should be a document to guide legislative decision making. An HIA is carried out prospectively and should be initiated during the planning stages of shale gas legislation. An effective HIA should aim to avoid or mitigate future impacts. The HIA should include the entire life cycle of the hydraulic fracturing process and all associated activities.

The HIA should employ a broad definition of health, as "a state of complete physical, mental and social well-being and not merely the absence of disease or infirmity (World Health Organization, 1946)." A successful HIA should be specific to the local community and should incorporate decision makers and potential stakeholders, including but not limited to property owners, industry, local regulators, local health agencies, and healthcare providers. The HIA can include the health of livestock and wildlife in addition to human health.

Components

- *Local, regional, and state level medical and demographic data.* These include electronic medical records, ideally with accompanying spatial data. Location information is important to determine residents proximity to potential sources of contamination, such as well pads or gas processing facilities. Demographic

[14] More information about Health Impact Assessments can be found at www.cdc.gov/healthyplaces/hia.htm

data can be used to identify potentially vulnerable groups within the population. Existing data sources include N.C. Detect for hospital and emergency room visits, N.C. Occupational Health and Safety for fatalities and catastrophes; N.C. Department of Transportation for road accidents; and workers compensation programs for worker injuries and illnesses.

- *Tracking of heath problems encountered in other states.* Monitoring outside of the state could provide early warning of heath problems which might occur in North Carolina in the future. Preventive action could then be taken.

- *Exposure information.* The HIA should analyze potential acute and chronic exposure pathways. Cumulative and individual chemical toxicity should be considered, to the extent possible without knowledge of specific chemical contaminant mixtures.

- *Psychological and other stressors.* The HIA should include all factors that could impact community health beyond direct chemical exposure, such as increased road traffic, light and noise pollution, and increased prevalence of sexually transmitted infections.

- *Economic analyses, including costs associated with health impacts.* These additional costs could include, for example, water remediation and increased asthma rates.

- *Common metrics.* Establishing standard metrics enables all parties contributing to the HIA to be on equal footing. These metrics should establish what should be monitored and should be tailored to the goals and priorities of the HIA.

B.6.3 Ongoing Health and Baseline Trend Analysis

North Carolina currently has limited surveillance for the types of medical conditions most likely to occur as a result of shale gas activities. The large influx of workers associated with shale gas could result in a change in the prevalence of sexually transmitted infections. In the most extreme scenario, if shale gas activities cause an increase in the amount of endocrine-disrupting chemicals in the environment, there could be increases in cancers, birth defects, and developmental disorders. The prevalence of other health conditions not currently being monitored also could change.

Evaluating potential health effects requires metrics that are easily quantifiable, comparable when evaluated by a variety of health care providers, and robust with a limited response rate.

6.3 Recommendations:

- *Use standard survey forms to establish baseline health effects.* These surveys can begin to build a database that will enable long-term tracking of a variety of medical conditions. These forms should be available to local health departments and administered as a routine part of visits at local doctors offices.

- *Use data types that are conducive to database tracking.* Use yes/no questions when possible. Provide units on forms so that all responses are consistent. Provide a standard list of health issues and symptoms that can be selected. Ideally, these data should have location information associated with them so that they can be geo-referenced.

- *Fund and mandate an organization within the N.C. State Center for Health Statistics for baseline health data analysis.*

B.6.4 Predictive Forecasting

Predictive forecasting prior to drilling should be included as part of a comprehensive HIA. Predictive models exist for risk assessment in situations in which information is limited (Hendren and Beaulieu, 2012). These models should be used to capitalize on the predictive power of available data.

Predictive forecasting models should be further improved with follow-up epidemiological studies. To the extent possible, these studies should examine correlations predicted by forecasting models. The goal of subsequent studies should be to revise the predictive model and update the available data.

Predictive models have limitations. Regulators and lawmakers should not rely on models alone without acknowledging the limitations of those models. Moreover, creating such models and doing the field work to validate them requires time and money. These models should be used to the extent that they are helpful in evaluating risk, but their implementation should not delay conducting an HIA before drilling occurs.

B.6.5 Public Awareness

Education can help ease the transition as a community begins to experience the effects of oil and gas drilling. The more residents know about the potential impacts of shale gas, the better prepared they are to make informed decisions about whether to lease land to drilling companies. Information should be available about the potential ecological and economic impacts of shale gas. Educational programs also can connect residents with potential avenues of assistance.

6.5 Recommendations:

- *Generate support and gain assistance from local community outlets.* Potential avenues for communication with residents include Area Health Education

Centers, the N.C. Cooperative Extension Service, local government Web sites, pharmacy brochures, information in libraries and schools, public service announcements, physicians, programs in retirement communities, and contact with support groups such as the Society of Asthma.

- *Provide pathways for communication among residents, officials, and industry representatives.* Sharing concerns early can help prevent future misunderstandings.

- *Collaborate with existing state agencies and resources.* These include the EPA Region 4 Office of Environmental Justice, the N.C. Division of Public Health Office of Minority Health, Legal Aid of North Carolina, the North Carolina Justice Center for Community Engagement, the Environmental Health State of Practice Committee, the N.C. Medical Society, and the N.C. Institute of Medicine.

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